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Concentration of H^2 Isotope

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A method is described of producing any desired concentration of the isotope of hydrogen, H^2, by electrolysis. Starting with twenty liters of water from an old commercial electrolytic cell and electrolyzing in four stages until only one-half of a cubic centimeter of water remained, this water had the specific gravity 1.073. Having shown that no large accumulation of the heavy isotopes of oxygen occurs and assuming that the density varies linearly with the fraction of H^2, 2/3 of the hydrogen in this water is H^2. It is shown that a further reduction of volume to one-quarter will give 99 percent H^2. In our electrolyses the percentage loss of H^1 is to the percentage loss of H^2 in the ratio of five to one. By two methods we have found 1 in 6500, as a provisional value for the concentration of H^2 in ordinary water.

SINCE the announcement[1] of our success in attaining a high concentration of hydrogen isotope has aroused some curiosity as to the methods that were employed, we shall describe here our procedure, although we should have liked first to have made a more scientific analysis of the various steps in the process, and although it seems probable that better methods of preparing the isotope will shortly be available. The fact is, the difference in properties between the two isotopes of hydrogen is so much greater than between any other pair of isotopes that in spite of the very small amount of H^2 present in ordinary hydrogen, several methods will lead to an almost complete separation of H^2 from H^1, as we have convinced ourselves by a number of preliminary experiments.

Being engaged some months ago in the separation of the isotopes of oxygen, we found it possible to follow small changes in the ratio of the isotopes in water by careful measurements of the density. By finding the temperature at which a 10 cc float will neither sink nor rise in ordinary pure water, and then finding the temperature at which this buoyancy balance is again established in a new sample of water, the specific gravity of that sample may be obtained with an accuracy of one part per million. At about 16°C a change of one part per million in density corresponds to a change of 0.006° in the temperature of the buoyancy balance. Of course, all the water samples must be carefully distilled and freed from dissolved air.

While we were engaged in the slow process of concentrating the oxygen isotopes we realized how much more interesting and important it would be to obtain the isotope of hydrogen which was discovered last year by Urey, Brickwedde and Murphy.[2] Since the concentration of H^2 in ordinary hydrogen has been recently estimated to be only about one part in thirty thousand, or less, it seemed hopeless to attempt such a separation unless a fractionating process could be

[1] Lewis, J. Am. Chem. Soc. **55**, 1297 (1933).

[2] Urey, Brickwedde and Murphy, Phys. Rev. **39**, 164 (1932).

obtained with an efficiency of an entirely different order of magnitude from that of the methods that have hitherto been used in the separation of isotopes. The more we considered the matter the more likely it seemed that such processes could be found, and this belief seemed to be corroborated by the discovery of Washburn and Urey[3] that the water in an old electrolytic cell contains an appreciably larger amount of H^2 than does ordinary water, although they did not determine the degree of concentration.

In this laboratory there is an electrolytic cell which has been operated for four years without any change except the occasional addition of distilled water to replace the water electrolyzed. We distilled some of the liquor from this cell and found it to have a specific gravity of 1.000034, as compared with ordinary water at the same temperature. This very startling increase in density, if due to a concentration of H^2 isotope, would indicate the presence of H^2 to the extent of one part in 3000, or ten times the amount which had been estimated to be present in ordinary water.

The theory of such a fractionation is simple. If the cell runs long enough to approach a stationary state, water being continually added to maintain a constant volume, then the composition of the electrolyte must approach a constant value. If α represents the percentage loss of H^2 divided by the percentage loss of H^1, then the ratio of H^2 to H^1 in the cell must ultimately approach a value $1/\alpha$ times as great as the initial value, and the composition of the evolved gases must approach that of the water added. Therefore our first experiment would seem to indicate that even if our electrolytic cell has nearly reached the equilibrium state, the value of α cannot be greater than 0.1. All this assumes that the evolved gases contain no water vapor. The fact that water vapor is lost in appreciable amount still further reduces the possible value of α.

Instead of adding water to keep the electrolyte at constant volume we may allow the total amount of electrolyte to change. If we call x_1 the amount of H^1 and x_2 the amount of H^2, then in each stage of the process

$$d \log x_2 = \alpha d \log x_1, \tag{1}$$

or, representing by x_1^0 and x_2^0 the initial amounts,

$$\log x_2/x_2^0 = \alpha \log x_1/x_1^0 \quad \text{or} \quad x_2/x_2^0 = (x_1/x_1^0)^\alpha. \tag{2}$$

Our next step was to carry out such an electrolysis. Some of the liquor from the large electrolytic cell was placed in a beaker with two plates of nickel as electrodes and was electrolyzed with a current of about 15 amperes until the volume had been reduced to about $\frac{2}{3}$ of the initial volume. The electrolyte was then distilled, and the increase in density over ordinary water was found to be fifty percent greater than before. This seemed once more to indicate that practically all of the H^2 was left behind.

These optimistic conclusions were suddenly overthrown by a simple calculation. Professor Giauque, who had been using the large electrolytic cell, was able to make a rough calculation of the total amount of water added to the cell during its four years of operation. Taking the original concentration of H^2 to H^1 as 1 to 30,000, it became evident that not more than one-third or one-quarter as much H^2 had ever been added to the cell as we were finding there. This discrepancy might be explained in one of two ways. Either the concentration of H^2 in ordinary water is much greater than had been supposed or our increase of density was not caused by the concentration of hydrogen isotope alone, but by concentration of the heavier isotopes of oxygen, which are initially present in much larger amount.

The possibility that any large accumulation of heavy oxygen had occurred was soon eliminated. Some of the water obtained in the electrolysis which we last described, and of which the temperature of buoyancy balance was 0.31° above that of ordinary water, was distilled in such a manner that the steam passed over hot iron wool where part of it was converted into hydrogen. The gases passed on into a condenser from which the water was returned to the still while the hydrogen continued into a tube containing hot copper oxide, where it was once more converted into water and was then condensed. After this process was complete a stream of hydrogen was passed through the hot iron

[3] Washburn and Urey, Proc. Nat. Acad. **18**, 496 (1932).

oxide, producing a second sample of water which contained all of the oxygen, while the first sample contained all of the hydrogen, of the initial water. This second sample had the density of ordinary water while the first, which contained only the hydrogen of the water under investigation, showed again a difference of 0.31° in buoyancy balance.

We were thus forced to the conclusion that the concentration of H^2 in ordinary water is much higher than has been usually estimated, approaching more nearly the value of 1 to 4500 first predicted by Birge and Menzel[4] from discrepancies in the atomic weight of hydrogen.

Our electrolytic experiment can now be explained by assuming first that the ratio of H^2 to H^1 in the hydrogen evolved from the cell is higher than we had supposed and second that in the calculation of concentration from density, correction must be made for an appreciable difference between the densities of ordinary water and of pure H^1H^1O. While these new conclusions show a poorer efficiency in the electrolytic separation, this is partly compensated by the higher initial concentration of H^2.

We therefore engaged at once in a process designed to reduce by electrolysis 10 liters of the water from the large electrolytic cell down to 1 cc or less. In a large glass tube were placed eight parallel nickel plates, each 55 sq. cm in area, connected alternately with the positive and negative leads, which were also of nickel. A copper coil was introduced through which cooling water flowed. A current of 250 amperes was used, although this was reduced in the later stages of the electrolysis, when the volume of the electrolyte became small. In order to avoid too high a concentration of electrolyte at the end of the run, we used one liter of $5M$ alkali from the large electrolytic cell, and 9 liters of water distilled from the same liquor.

At the end of five or six days the electrolyte was reduced to one liter. Of this, ninety percent was placed in a bath at 0°C, while CO_2 was allowed to bubble through it until all the alkali was converted to normal Na_2CO_3, indigo carmine being used as indicator. This solution was then distilled from a copper kettle which could be heated finally to drive over all the water of crystallization. The 900 cc thus obtained, together with the 100 cc of alkaline solution reserved from the preceding electrolysis, were placed in a smaller but similar cell and electrolyzed to a volume of about 100 cc. This in turn, employing the same procedure as before, was electrolyzed in a third still smaller cell until it was reduced to 10 cc. In the fourth very small cell, which, instead of having a cooling coil, was surrounded by ice water, the volume of electrolyte was reduced to a little over half a cubic centimeter. This liquid, treated with carbon dioxide, was distilled in a vacuum into a small container. The water thus obtained was found by means of a small picnometer to have the specific gravity 1.035; in other words, 31.5 percent of all the hydrogen in this water is H^2.

In the next series of experiments changes were made in the first and the last electrolytic concentrators. In the first, the 10 liter glass cylinder was replaced by a 20 liter cylinder of monel metal with external cooling, and the current was increased to 400 amperes. In the last concentrator provision was made for saving the evolved gases. These were recombined on platinized asbestos, thus giving water containing several percent of H^2.

In this second run, concentrating from 20 liters to 0.5 cc, we obtained water of specific gravity 1.073. Accordingly, in this water 65.7 percent of the hydrogen is H^2. While our previous experiment showed conclusively that there is no large change in the ratio of oxygen isotopes in our electrolytic process, and while spectroscopic analysis has shown that the hydrogen obtained from this sample of water contains over fifty percent of H^2, two things must be done before we can, with certainty, obtain the composition from the density. First, we must subject this water to the process that we have described, which would free it from oxygen in which the isotope ratio may have changed, and second, we must prove that the density varies linearly with the composition. These two experiments have not yet been completed.

In our whole process of concentration we have attempted to adhere as nearly as possible to the conditions of our large commercial electrolytic cell until we could, by theory or experiment,

[4] Birge and Menzel, Phys. Rev. **37**, 1669 (1931).

ascertain the best conditions for electrolytic separation. Thus all of our electrodes and leads were made of pure nickel. However, during the course of the experiments stray currents caused the transfer of copper from the cooling coils, and we have suspected that this copper plating may have slightly diminished the efficiency of the electrolytic separation, but we have as yet no proof of this. We have attempted to keep the temperature during electrolysis below 35°C, chiefly to avoid loss of water by evaporation, but partly also because it seemed likely that the efficiency of separation would be higher at low temperatures. Here again we have made no systematic efforts to prove the correctness of this view.

By determining the density of the water in the various stages of concentration we have attempted to determine the efficiency of the electrolytic separation. While there seemed to be some individual variations, all the results agree pretty closely with the assumption that the value of α in Eq. (1) is 0.20. In other words, under equivalent conditions, five times as much H^1 as H^2 is evolved.

According to this figure, if the water containing 65.7 percent H^2 were reduced by electrolysis to one-quarter of its volume, it would contain 99 percent of H^2. We have, however, postponed making this experiment until larger amounts of heavy water become available.

There is not much that can be said at present regarding the theory of the electrolytic fractionation. It is evident that under the conditions of our experiments there is, between the two isotopes, a difference in the electrical polarization at the cathode amounting to four centivolts. Assuming that this represents chiefly a difference in rates, rather than in the true electrode potentials, it is hard to guess how much of this difference in rates is due to the difference in mobility of the two hydrogen ions, to the difference in rates of diffusion of the two atomic species in the nickel surface, and to a difference in rates of recombination of the atoms. These questions are now under investigation. In addition Professor Heyrovsky is planning to make direct determinations of the overvoltage of the two isotopes.

In conclusion, let us make an estimate of the amount of the heavy hydrogen isotope in ordinary water, realizing that samples from different sources may vary considerably. There are two simple ways of making this determination. By successive electrolyses, collecting and recombining the evolved gases, we may approximate to pure H^1H^1O and find the difference in density between it and ordinary water. On the other hand, we may concentrate ordinary water in an electrolytic cell of known efficiency and find the increase in density. Preliminary measurements by both methods indicate that in Berkeley city water there is one part of H^2 to about 6500 parts of H^1.

Theoretical Considerations Concerning the Separation of Isotopes

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The relative importance of effusion processes, the half quanta due to van der Waals forces, and half quanta associated with homopolar bonds is considered with respect to the question of the separation of isotopes. Specific reaction rate constants for various isotopic molecules in effusion processes have been calculated. It is shown that only in the neighborhood of liquid hydrogen temperatures or lower are the half quanta due to van der Waals forces important. Specific reaction rate constants involving the zero point energy of homopolar molecules have been calculated for various isotopic molecules, principally those in which a hydrogen atom is one constituent, at temperatures of 20°K, 90°K, and 273°K. The advantage of working at as low a temperature as possible is rendered apparent. Even at ordinary temperatures the differences in the constants are in general much greater than in the case of effusion or van der Waals processes. A general equation is derived relating the concentration of the light and heavy isotopes, valid for any one of the three processes considered.

RECENTLY theoretical discussions of the effect of zero point energy on reaction rates, with particular reference to the question of separating the hydrogen isotopes have been given.[1] This general question now possesses additional interest as a result of recent experiments.[2]

Lewis reports the obtaining of water of specific gravity 1.035, presumably by electrolysis. Taylor, Gould and Bleakney obtained a 5-fold increase in concentration of H^1-H^2 over that present in ordinary hydrogen by desorbing hydrogen from an active charcoal surface at liquid air temperatures. It is the purpose of this paper to consider the subject in greater detail and to present the results of some calculations which show maximum differences in specific reaction rate constants to be expected, at various temperatures, in reactions involving various isotopic molecules.

We shall first consider effusion processes. The rate at which a molecule of molecular weight M effuses through an orifice is proportional to its velocity component in the direction normal to the orifice. This in turn is inversely proportional to the square root of the molecular weight, as is shown by kinetic theory. The ratio of the specific rates of effusion of gaseous molecules of molecular weights M_1 and M_2 will, therefore, be proportional to $(M_2/M_1)^{\frac{1}{2}}$. This ratio is of course independent of temperature.

Consider a gas containing two isotopic molecules of concentration (X) and (Y) effusing through an orifice. One can think of the two processes as independent unimolecular reactions in the ordinary way and obtain for the relative concentration of the isotopes the expression $(Y_0)/(Y)=(X_0/X)^{(M_x/M_y)^{\frac{1}{2}}}$. The subscript 0 denotes the initial concentration. In column three of Table I is given the relative increase in concentration of the heavy isotope to be expected in the remaining gas when the pressure is reduced to the fraction of the initial pressure indicated in column two.

TABLE I.

Gas	Pressure drop	Relative increase in H^1-H^2
H^1-H^1	1/100	2.28
H^1-H^2	1/10	1.52
	1/5	1.34
$O^{16}-O^{16}$	1/100	1.15
$O^{16}-O^{18}$	1/10	1.07
	1/5	1.05
$N^{14}-N^{14}$	1/100	1.08
$N^{14}-N^{15}$	1/10	1.04
	1/5	1.03

[1] Cremer and Polanyi, Zeits. f. physik. Chemie **19B**, 443 (1932); Eyring, Proc. Nat. Acad. Sci. **19**, 78 (1933).

[2] Washburn and Urey, Proc. Nat. Acad. Sciences **18**, 496 (1932); G. N. Lewis, J. Am. Chem. Soc. **55**, 1297 (1933); H. S. Taylor, Gould and Bleakney, Phys. Rev. **43**, 496 (1933); Washburn, Smith and Frandsen, J. Chem. Phys. **1**, 288 (1933).

In the experiments of Taylor, Gould and Bleakney an initially adsorbed 5025 cc, desorbed to 35 cc, showed a 3-fold increase in the heavy isotope, while with 5715 cc adsorbed a reduction to 90 cc in a two stage process showed a 5-fold increase. It is seen from Table I that the results cannot be accounted for by an effusion process alone because the 5715 cc to 90 cc reduction should produce, at most, a 2-fold increase, in contrast to the 5-fold actually obtained. It is therefore clear that other factors must play an important rôle. If the molecules are not initially free but are escaping from a solid or liquid surface the forces with which they are held will further modify the specific rate for the two isotopes. To estimate the effect of the van der Waals forces in a liquid we shall use the empirical potential functions of Lennard Jones.[3]

For the potential energy between two hydrogen molecules as a function of the distance, r, between them, he gives

$$E=(48.9\times10^{-115})/13\tfrac{1}{3}r^{13\frac{1}{3}} - (15.6\times10^{-45})/4r^{4} \text{ ergs/molecule.}$$

One might object to the use of this function for this purpose on the grounds that it was designed to explain observed results on the basis of classical mechanics but a detailed consideration of the potential energy between hydrogen molecules using perturbation theory gives essentially the same results.[4]

Consider the removal to infinity of a hydrogen molecule initially at a distance r from a liquid hydrogen surface. Assume the molecules of the liquid are, on the average, at the corners of a cube, the size of which, calculated from the observed density of the liquid, is 3.6A. The van der Waals attraction of the molecule will be the sum of the attractions of the molecules in the liquid. The 196 nearest neighbors give the energy E presented in Table II, for distances, along the normal to the surface, equal to r. The contribution to the energy of the remaining molecules is small.

We fit the parabola $y-a=\frac{1}{2}k(x-b)^2$ to the values in Table II and use for the vibrational frequency $\omega=(1/2\pi)(k/\mu)^{\frac{1}{2}}$, where we take for the reduced mass of the oscillator consisting of one molecule vibrating against the surface, the mass of the molecule. In this way we obtain for the oscillators H^1H^1 and H^1H^2 half quanta of 56.3 and 46.0 calories/mol, respectively. This gives a difference of 10.3 calories/mol as the difference between the half quanta so that, at the boiling point of liquid hydrogen, 20°K, the relative specific rates of desorption of H^1H^1 and H^1H^2 due to this energy alone is $e^{10.3/2\times20}=1.29$.

TABLE II.

r (A)	3.20	3.40	3.60
E (ergs/mol)	-51.66×10^{8}	-53.96×10^{8}	-51.77×10^{8}

In considering the actual rate of escape from the surface this factor should probably also be multiplied by the factor arising from the difference in velocities for the effusion process discussed above.

Thus we see that the van der Waals forces in the evaporation of liquid hydrogen will materially increase the concentration of the heavier isotope in the residue.

We now make a rough estimate of the half quantum for van der Waals adsorption of a hydrogen molecule on charcoal at liquid air temperatures. For homopolar molecules the heat of dissociation, D, is approximately proportional to the force constant k for a wide variety of molecules as is shown by the fact that the constant a of the Morse equation varies but little from molecule to molecule. This same approximate proportionality holds for the van der Waals potential holding two molecules together. This is readily seen by a consideration of the empirical curves given by Lennard-Jones. For the evaporation process of any molecule held to a liquid or solid surface by van der Waals forces the force constant will remain about proportional to D for different surfaces and different molecules. A test of this assumption for the evaporation of liquid He, H_2, Ne, N_2 and A indicates that the force constant k does not rise quite as rapidly as the boiling point.

In the table k is the force constant for the oscillator molecule-surface. These values of k

[3] Fowler, *Statistical Mechanics*, Chapter X, Cambridge Univ. Press, 1929.

[4] Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

were calculated in the manner described for H_2, using the constants given by Lennard-Jones for the equation

$$E=\lambda r^{-n+1}/(n-1)-\mu r^{-m+1}/(m-1).$$

ΔH_v is the heat of vaporization and T_β the boiling point. The value of n used was $14\frac{1}{3}$ and of m used was 5.

For the evaporation of any molecule held to a liquid or solid surface we may expect Trouton's rule to hold, namely that the heat of vaporization is proportional to the absolute temperature at which the vapor pressure is atmospheric. Consequently we expect $\frac{1}{2}h\omega=(c/2\pi)(T/M)^{\frac{1}{2}}$ to hold roughly for all substances. If c is chosen to fit for liquid hydrogen the calculated half quanta for substances with higher boiling points will probably be too high. As before, M is the reduced mass. Thus the difference in the half quanta for H^1H^1 and H^1H^2 at liquid hydrogen temperatures is 10.3 calories while for the same molecules boiling from charcoal at liquid air temperatures a difference of about $10.3(90/20)^{\frac{1}{2}}=21.85$ calories or less is to be expected for molecules held by van der Waals forces. This gives for the ratio of the specific reaction rates at 90°K the value 1.13, which is less than the difference due to rates of effusion. Because of the larger reduced masses van der Waals forces will play an even less important rôle for substances other than hydrogen.

It thus seems clear that Urey, Brickwedde and Murphy's[5] separation of the hydrogen isotopes at the triple point (insofar as it departs from an equilibrium process) was due to van der Waals forces, helped by differences in the effusion rates of the isotopes, while the results of Taylor, Gould and Bleakney[6] at liquid air temperatures can only be explained on the basis of surface forces with greater associated half quanta than those of the van der Waals type.

When the hydrogen molecules instead of being held by the long range polarization or van der Waals forces are dissociated and form homopolar bonds with atoms in the surface the corresponding half quanta are much larger. In Table III are

TABLE III.

Gas	He	H_2	Ne	N_2	A
k	34	186	441	238	740
$k/\Delta H_v$	1.4	0.87	1.1	0.18	0.49
k/T_β	7.9	9.2	12.9	3.0	8.5

tabulated values for the extreme case where the surface atom and the adsorbed atom behave as isolated oscillators. The actual half quanta for surfaces will no doubt in general be smaller but the table should help in the selection of a desirable surface for separation of isotopes by either desorption or electrolysis.

The ratios of the factors $e^{E/RT}$ for light and heavy isotopes in columns 3, 4 and 5 give the relative specific rates at 20°, 90° and 273°K. The advantage of using low temperatures becomes strikingly obvious. Thus, for $C^{12}-H^1$ and $C^{12}-H^2$ these ratios are 1.3×10^{12}, 5.0×10^{2}, and 7.7 at 20, 90 and 273°K respectively. (Table IV.)

The calculations for electrolysis or desorption presuppose reaction processes with identical potential barriers for both isotopes. The chief difference in relative rates arises from the greater half quanta of the lighter isotope. Consider the case where hydrogen atoms are being desorbed from a solid surface to make hydrogen molecules. This can occur by two light atoms coming off together, or a light and heavy one, or finally by two heavy ones combining. If we represent the concentration of heavy isotope by y, and light ones by x, we have the two simultaneous equations,

$$-dx/dt=kx^2+ksxy; \quad -dy/dt=ksxy+ks^2y^2. \quad (1)$$

The two equations become identical if we take $y=cx^s$ so that this relationship is maintained between light and heavy isotopes. Evaluating c by putting in the initial concentrations x_0 and y_0 we obtain

$$y/y_0=(x/x_0)^s. \quad (2)$$

Of course $s=e^{-\Delta E/RT}$ where ΔE is the difference between the zero point energy for an oscillator composed of a surface atom and H^1 and for a second oscillator composed of a surface atom and H^2. Further, s is a proper fraction.

It is interesting to observe that (2) is the same relationship obtained for the separation by

[5] Urey, Brickwedde and Murphy, Phys. Rev. **39**, 164 (1932).

[6] Taylor, Gould and Bleakney, Phys. Rev. **43**, 496 (1933).

TABLE IV.

Bond	$\frac{1}{2}h\nu$ (kg.cal.)	$e^{E/20R}$	$e^{E/90R}$	$e^{E/273R}$	Bond	$\frac{1}{2}h\nu$ (kg.cal.)	$e^{E/20R}$	$e^{E/90R}$	$e^{E/273R}$
H^1-H^1	6.2	7.2×10^{67}	1.2×10^{15}	9.4×10^{4}	$Ni-H^1$	2.3	5.7×10^{24}	3.2×10^{5}	6.5×10^{1}
H^1-H^2	5.4	5.9×10^{58}	1.2×10^{13}	2.0×10^{4}	$Ni-H^2$	1.6	4.5×10^{17}	8.4×10^{3}	2.0×10^{1}
H^2-H^2	4.4	9.9×10^{47}	4.6×10^{10}	3.3×10^{3}	$Au-H^1$	3.2	7.8×10^{34}	5.7×10^{7}	3.6×10^{2}
$O^{16}-H^1$	5.2	5.9×10^{56}	4.1×10^{12}	1.4×10^{4}	$Au-H^2$	2.3	5.4×10^{24}	3.1×10^{5}	6.5×10^{1}
$O^{16}-H^2$	3.8	2.1×10^{41}	1.5×10^{9}	1.1×10^{3}	$Zn-H^1$	2.3	1.1×10^{25}	3.7×10^{5}	6.8×10^{1}
$O^{17}-H^1$	5.2	4.7×10^{56}	3.9×10^{12}	1.4×10^{4}	$Zn-H^2$	1.6	7.0×10^{17}	9.2×10^{3}	2.0×10^{1}
$O^{17}-H^2$	3.8	1.5×10^{41}	1.4×10^{9}	1.0×10^{3}	$Hg-H^1$	2.0	1.7×10^{22}	8.7×10^{4}	4.3×10^{1}
$O^{18}-H^1$	5.2	3.9×10^{56}	3.8×10^{12}	1.4×10^{4}	$Hg-H^2$	1.4	5.2×10^{15}	3.1×10^{3}	1.4×10^{1}
$O^{18}-H^2$	3.8	1.1×10^{41}	1.3×10^{9}	1.0×10^{3}	Hg^+-H^1	2.9	1.9×10^{31}	8.9×10^{6}	2.0×10^{2}
$C^{12}-H^1$	4.2	2.8×10^{45}	1.3×10^{10}	2.1×10^{3}	Hg^+-H^2	2.0	1.3×10^{22}	8.2×10^{4}	4.2×10^{1}
$C^{12}-H^2$	3.1	2.2×10^{33}	2.6×10^{7}	2.8×10^{2}	$O^{16}-O^{16}$	2.25	3.8×10^{24}	2.9×10^{5}	6.3×10^{1}
$C^{13}-H^1$	4.1	2.0×10^{45}	1.2×10^{10}	2.1×10^{3}	$O^{16}-O^{17}$	2.22	1.7×10^{24}	2.4×10^{5}	6.0×10^{1}
$C^{13}-H^2$	3.0	1.5×10^{33}	2.4×10^{7}	2.7×10^{2}	$O^{16}-O^{18}$	2.19	7.6×10^{23}	2.0×10^{5}	5.6×10^{1}
$Be-H^1$	3.0	4.6×10^{32}	1.8×10^{7}	2.5×10^{2}	$O^{17}-O^{18}$	2.15	3.2×10^{23}	1.7×10^{5}	5.3×10^{1}
$Be-H^2$	2.2	1.7×10^{24}	2.4×10^{5}	6.0×10^{1}	$O^{18}-O^{18}$	2.12	1.5×10^{23}	1.4×10^{5}	5.0×10^{1}
$Al-H^1$	2.4	1.2×10^{26}	6.3×10^{5}	8.2×10^{1}	$N^{14}-N^{14}$	3.35	4.0×10^{36}	1.4×10^{8}	4.8×10^{2}
$Al-H^2$	1.7	5.9×10^{18}	1.5×10^{4}	2.4×10^{1}	$N^{14}-N^{15}$	3.29	9.4×10^{35}	9.9×10^{7}	4.3×10^{2}
$Fe-H^1$	1.9	3.6×10^{20}	3.7×10^{4}	3.2×10^{1}	$N^{15}-N^{15}$	3.23	2.3×10^{35}	7.2×10^{7}	3.9×10^{2}
$Fe-H^2$	1.3	4.5×10^{14}	1.8×10^{3}	1.2×10^{1}	$Cl^{35}-Cl^{35}$	0.80	5.9×10^{8}	8.9×10^{1}	4.4
$Pt-H^1$	1.7	7.6×10^{18}	1.6×10^{4}	2.4×10^{1}	$Cl^{35}-Cl^{37}$	0.79	4.6×10^{8}	8.4×10^{1}	4.3
$Pt-H^2$	1.2	2.4×10^{13}	9.4×10^{2}	9.6	$Cl^{37}-Cl^{37}$	0.78	3.4×10^{8}	7.9×10^{1}	4.2
$Cu-H^1$	2.7	3.4×10^{29}	3.6×10^{6}	1.5×10^{2}					
$Cu-H^2$	1.9	1.1×10^{21}	4.8×10^{4}	3.5×10^{1}					

effusion or by van der Waals forces if s is interpreted, there also, as the ratio of the specific rates for the light and heavy isotopes. Thus the determination of the efficacy of separation by the three processes reduces to comparing the ratios of the specific reaction rates.

It is of course possible to distinguish experimentally the first order desorption of molecules held by van der Waals forces and the desorption of atoms which obey the Eq. (1). Eqs. (1) become after the substitution of (2)

$$\int_{x_0}^{x} \frac{dx}{x^2+[s(y_0/x_0^s)]x^{s+1}} = -kt,$$

and for y_0/x_0 very small this behaves for a considerable time as a typical second order reaction.

From Table II we see that the separation of other isotopes than those of hydrogen should at least be more readily attained by reactions at suitably low temperatures than by a straight diffusion process. The particular virtue of electrolysis is that, even though the activation energy (overvoltage) may be considerable, still, by applying a suitable potential, the reaction may be made to go at low temperatures. The same object may be accomplished by carrying out reactions photochemically. With this in mind Taylor and Gould are carrying out the hydrogen and chlorine reaction at suitably low temperatures. Of course any other agent than light which will supply atoms at low temperatures would do equally well.

Many reactions which in a laboratory would proceed too slowly at ordinary temperatures to secure the desired separation may have occurred geologically where an entirely different time scale is available. Low temperature mineralizing and erosion processes immediately suggest themselves.

Since all chemical reactions having a positive temperature coefficient will go about half as fast, or less, at ordinary temperatures with the heavy as with the light hydrogen isotope it will be possible to single out such reactions in biological processes.

Separation of isotopes due to equilibrium differences have been frequently discussed and require no additional consideration here. In general such separations will be less efficient than the corresponding dynamic processes. The heavier isotope approaches equilibrium more slowly from both directions.

CONCLUSIONS

Detailed calculations of the rôle of zero point energy in the separation of isotopes by dynamic processes are given. Apparently only in the

neighborhood of liquid hydrogen temperatures are the half quanta due to van der Waals forces important. Processes which involve the breaking of homopolar bonds at moderate or low temperatures are far more efficient than effusion processes. Any agents which provide atoms at low temperatures which then enter into subsequent reactions are particularly effective. Familiar examples are catalysts, light, electric discharges, and electrolysis.

Molecular Vibrations of Three Particle Systems with Special Applications to the Ethyl Halides and Ethyl Alcohol

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The vibrational potential of polyatomic molecules is discussed in the light of the theory of directed valence. Andrews' assumptions of "valence forces" are seen to be rather special, but at the same time are fairly good approximations under certain conditions. The normal vibrations of three body systems are calculated for the potential function

$$V=\tfrac{1}{2}[k_1(\Delta r_1)^2+k_2(\Delta r_2)^2+k_3(r_1^{0^2}+r_2^{0^2})(\Delta\gamma)^2]$$

with r_1, r_2 radial coordinates and γ an angular one. The potential terms proportional to $\Delta r_1\Delta r_2$, etc., are treated as perturbations. These calculations are applied to the ethyl halide and ethyl alcohol molecules by considering the CH_3, CH_2 and OH groups as dynamic units. Force constants were determined which gave approximately the experimental frequencies. The calculation of the normal modes of vibration illustrate the approximate validity of the designation of the modes of vibration of *unsymmetrical* three body systems as two independent radial motions and an angular motion.

I. Introduction: Relation of Directed Valence to Vibrational Potentials

IN a recent study of the infrared absorption spectra of the ethyl halides (CH_3CH_2Cl, CH_3CH_2Br, CH_3CH_2I) Cross and Daniels[1] suggested for each of the fundamental bands a type of motion which was believed to represent the chief characteristic of the normal modes of vibration involved. Three of these types of motion (types F_5, F_7, F_8 of reference 1) may be considered as the characteristic modes of a three body system in which the units are the halogen atom, the CH_3 group, and the CH_2 group. These were given as illustrated in Fig. 1. The experimental evidence for each may be summarized briefly as: (1), the occurrence of a characteristic frequency whenever the group $-CH_2X$ is present; (2), the occurrence in all the ethyl halides of a frequency nearly equal to that of a strong Raman line of ethane; and (3), the low value of the bending frequency in the ethyl halides and the fact that no such low frequency is found in the methyl halides.

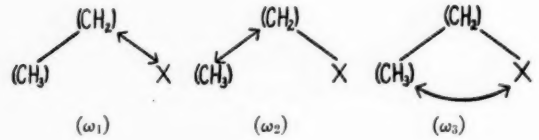


FIG. 1.

Cross and Daniels also noted the apparent absence of the frequency characteristic of the H_3C-CH_2 bond in the case of ethyl alcohol (CH_3CH_2OH). They suggested that the symmetry of the molecule resulted in a strong interaction between the different types of motion in such a way that a given frequency could not be assigned to a type of motion involving only a part of the molecule. (The word symmetry, as used here, applies to the equality of the masses attached by the central atom. In ethyl alcohol the attached masses are 15 and 17 on the atomic weight scale.) The same should, incidentally, be true for ethyl fluoride.

The purpose of this paper is to calculate the normal modes of vibration of three body systems analogous to each of the ethyl halides and to ethyl alcohol. The masses, dimensions and normal frequencies shall correspond to those of the molecules, considering the CH_3 group and the CH_2 group as units (Fig. 1). It is reasonable to assume that the hydrogen atoms, by virtue of their small mass and the strong forces holding them to the carbon atoms, do not produce any first order deviations in the dynamical behavior of the molecules from that of three body systems in the vibrations we are considering. Hence the

[1] P. C. Cross and F. Daniels, J. Chem. Phys. **1**, 48 (1933).

results of this calculation should be a qualitative test of the accuracy of the above suggestions.

Most of the previous work on the small vibrations of triatomic molecules has dealt with symmetrical systems, i.e., systems of the type XY_2.[2, 3, 4, 5] Radakovic[6] has, however, given a general solution for the potential function

$$V=\tfrac{1}{2}[c_{13}(\Delta r_{13})^2+c_{23}(\Delta r_{23})^2+c_{12}(\Delta r_{12})^2], \quad (1)$$

in which Δr_{ij} is the displacement of the distance between the particles i and j from the equilibrium distance. Instead of (1) we shall use the potential function

$$V=\tfrac{1}{2}[k_1(\Delta r_1)^2+k_2(\Delta r_2)^2+k_3(r_1{}^{0^2}+r_2{}^{0^2})(\Delta\gamma)^2]. \quad (2)$$

The significance of the coordinates is clear from Fig. 2. The coordinate γ is an angle rather than

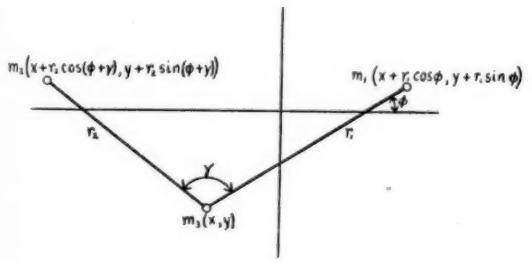


FIG. 2.

a distance, while r_1 and r_2 are identical with r_{13} and r_{23} of (1). The equilibrium values of r_1, r_2 are denoted by $r_1{}^0$, $r_2{}^0$. The factor $r_1{}^{0^2}+r_2{}^{0^2}$ is inserted in (2) to make k_3 dimensionally similar to k_1, k_2; otherwise no direct significance could be attached to comparison of the numerical values of the various force constants.

A system obeying (2) is often called a "valence force system" in the literature. Eq. (2) has a more reasonable form of the potential function than (1) if the directional valence of the central atom is more important than the repulsion between the attached atoms.

The most general form of the potential function for small, i.e., harmonic, vibrations would include terms proportional to $\Delta r_1\Delta r_2$, $\Delta r_1\Delta\gamma$, and $\Delta r_2\Delta\gamma$ (or terms proportional to $\Delta r_{12}\Delta r_{13}$, etc., in (1)). In writing (1) and (2) we have assumed only three atoms, but the extensions to molecules with an arbitrary number of atoms are obvious, and our discussion on cross-terms in the next few paragraphs is not restricted to triatomic molecules.

Actually the terms proportional to $\Delta r_1\Delta\gamma$ and $\Delta r_2\Delta\gamma$ do not vanish completely. In the first place, the theory of directional valence requires that the angular equilibrium positions be somewhat modified when one of the bonds is stretched or contracted. This has been demonstrated by one of the writers in an article in this journal.[7] It was there shown, for instance, that in tetravalent carbon compounds, quite irrespective of repulsions between the attached atoms, the tetrahedral angles 109.5° should be somewhat modified when the four bonds are not of equal intensity. The bonds must be considered unequal not only when the four attached atoms are not identical, but also in symmetrical molecules such as CX_4 when an atom X is moved radially from its equilibrium position, so that the symmetry is lost. Hence the terms in $\Delta r_1\Delta\gamma$ and $\Delta r_2\Delta\gamma$ cannot disappear, for absence of such terms implies that the equilibrium angles are unmodified by small radial displacements. However, it is probably true that the equilibrium angles do not vary greatly from 109.5° even when the bonds are of unequal intensity or even when the central atom is not tetravalent. (Witness, for instance, the equilibrium angle in the neighborhood of 100° in the case H_2O. Of course CO_2 is collinear and so has an angle of 180°, but here there is the complication of double bonds, to which our discussion does not apply.) This is a very happy circumstance, for otherwise any discussion of angular structure in molecules would needs be much more difficult than in reality. The reason why 109.5° is usually not far amiss is the following: for a structure C–X–Y involving a single valence angle X–C–Y the best value of the angle was shown by one of us[7] to

[2] N. Bjerrum, Verh. d. D. Phys. Ges. **16**, 737 (1914).
[3] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).
[4] R. C. Yates, Phys. Rev. **36**, 555 (1930).
[5] K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* (and references therein) Julius Springer, Berlin, 1931.
[6] M. Radakovic, Wien. Ber. **139**, 107 (1930).
[7] J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933); (cf. especially Sections 5 and 6).

vary from 90° to 180° depending on the relative importance of the bonds emanating from the $2s$ and $2p$ states of the C atom. If the $s-p$ interplay were the only important thing, the best angle would be 180°, while 90° would be required for pure p-bonding. Actually, the p-bonding is perhaps dominant, so that the best angle is nearer 90° than 180°. In a compound of the form CWXYZ, each angle W–C–X, W–C–Y, . . . Y–C–Z has an optimum value between 90° and 180° as far as its own particular directional valence is concerned. These values are in general not compatible, and so must be somewhat modified, with the most powerful directional valences, of course, in general favored at the expense of the others. The important thing, however, is that the best value for any individual angle is between 90° and 180°, and so never extremely different from 110° even when the bonds are of unequal intensity. Hence the alteration in equilibrium angle upon stretching or contracting a bond is probably very small, and so the terms in $\Delta r_1\Delta\gamma$ and $\Delta r_2\Delta\gamma$ originating from this cause are probably subordinate. A term in $\Delta r_1\Delta r_2$ is, in principle, required because the configuration of the C atom is somewhat modified by any alterations in position of the attached atoms, so that when one bond is stretched, the equilibrium radial values for other bonds are altered. Such terms, however, are probably very small. Otherwise particular bonds would not have nearly invariant vibration frequencies in a wide range of compounds.

In the preceding paragraph we have considered only the effect of the valences emanating from the central atom. A more important cause of the "cross-terms" proportional to $\Delta r_1\Delta r_2$, $\Delta r_1\Delta\gamma$, $\Delta r_2\Delta\gamma$ is perhaps the repulsions between the attached atoms. If r_{12} be the distance between the attached atoms, this repulsive energy is a function of the single argument r_{12}, and will generate cross-terms since $(\Delta r_{12})^2=[a\Delta r_1+b\Delta r_2+c\Delta\gamma]^2$. The cross-terms originating from this cause will be computed in the next paper for the H_2O molecule. It will be found that these terms are sufficiently small to let (2) be the dominant part of the potential energy, but are at the same time by no means negligible, and are sufficiently great to make purely fortuitous any exact agreement with experiment achieved by using a potential of the form (2). For this reason, it has seemed desirable to give in Section V a theory for treating the cross-terms as a perturbation superposed on (2).

When the specification of the molecule requires several angular coordinates γ_1, γ_2, $\cdots$, the vibrational potential will in general contain cross-terms proportional to $\Delta\gamma_1\Delta\gamma_2$, etc., because the equilibrium position of any given valence angle is modified by angular displacements in other bonds. Such cross-terms do not arise in the cases treated in this or the following paper, because we restrict our attention to effectively triatomic molecules, where only one angular coordinate is necessary. The well-known assumptions of Andrews[8] concerning molecular vibrations appear to be tantamount to assuming that all the various types of cross-terms are negligible. Hence his hypotheses are rather restrictive. We have seen that the quantum mechanics of directed valence requires that the cross-terms, at least in $\Delta r\Delta\gamma$, are not excessive, and this probably explains why Andrews' theory has been attended with some qualitative success.

After our calculations were completed an article by Lechner[9] appeared, likewise giving the derivation of the characteristic frequencies for the potential function (2). His paper does not give the details of his derivation or analyze the perturbing effect of cross-terms and so it seems advisable to include the mathematical analysis which we used, as well as the applications, which are to different molecules than those studied by Lechner. Also, we believe the Lagrangian function (6) which we give may be useful for other three body problems besides the ones which we consider. In particular the kinetic energy terms of (6) would be useful if one desired to carry through a calculation in which the oscillations were not infinitesimal, so that the method of normal coordinates could not be used.

[8] D. H. Andrews, Phys. Rev. **36**, 544 (1930).
[9] F. Lechner, Monatshefte f. Chemie **61**, 385 (1932).

II. The Problem of the Three Body Systems

The kinetic energy in the Cartesian coordinate system is

$$T=\tfrac{1}{2}m_1[\{\dot{x}+\dot{r}_1\cos\phi-r_1\dot{\phi}\sin\phi\}^2+\{\dot{y}+\dot{r}_1\sin\phi+r_1\dot{\phi}\cos\phi\}^2]$$
$$+\tfrac{1}{2}m_2[\{\dot{x}+\dot{r}_2\cos(\phi+\gamma)-r_2(\dot{\phi}+\dot{\gamma})\sin(\phi+\gamma)\}^2+\{\dot{y}+\dot{r}_2\sin(\phi+\gamma)+r_2(\dot{\phi}+\dot{\gamma})\cos(\phi+\gamma)\}^2]$$
$$+\tfrac{1}{2}m_3[\dot{x}^2+\dot{y}^2]. \tag{3}$$

Let us take the origin of these coordinates at the center of mass, which we may suppose to be stationary. Then x and y may be eliminated through the relations

$$\sum m_i x_i=\sum m_i y_i=0, \tag{4}$$

and the resulting Lagrangian function is

$$L=T-V=\tfrac{1}{2}\mu_1[\dot{r}_1^2+r_1^2\dot{\phi}^2]+\tfrac{1}{2}\mu_2[\dot{r}_2^2+r_2^2\dot{\phi}^2+2r_2^2\dot{\phi}\dot{\gamma}+r_2^2\dot{\gamma}^2]$$
$$-\mu_3[\dot{r}_1\dot{r}_2\cos\gamma+r_1\dot{r}_2\dot{\phi}\sin\gamma-r_2\dot{r}_1(\dot{\phi}+\dot{\gamma})\sin\gamma+r_1r_2(\dot{\phi}^2+\dot{\phi}\dot{\gamma})\cos\gamma]$$
$$-\tfrac{1}{2}[k_1(\Delta r_1)^2+k_2(\Delta r_2)^2+k_3(r_1^{0^2}+r_2^{0^2})(\Delta\gamma)^2], \tag{5}$$

where
$$\mu_1=\frac{m_1m_2+m_1m_3}{m_1+m_2+m_3},\quad \mu_2=\frac{m_1m_2+m_2m_3}{m_1+m_2+m_3},\quad \mu_3=\frac{m_1m_2}{m_1+m_2+m_3}.$$

Since ϕ does not occur explicitly in L, it is ignorable and $\dot{\phi}$ may be eliminated by solving $\partial L/\partial\dot{\phi}=P$ for $\dot{\phi}$ and substituting this value of $\dot{\phi}$ in the function[10] $R=L-\dot{\phi}(\partial L/\partial\dot{\phi})$. Since P is the angular momentum of the system, it will be taken as zero inasmuch as, for our purposes, the system may be considered devoid of rotation. This gives

$$R=\tfrac{1}{2}[\mu_1-\rho\mu_3^2r_2^2\sin^2\gamma]\dot{r}_1^2+\tfrac{1}{2}[\mu_2-\rho\mu_3^2r_1^2\sin^2\gamma]\dot{r}_2^2+\tfrac{1}{2}\rho r_1^2r_2^2[\mu_1\mu_2-\mu_3^2\cos^2\gamma]\dot{\gamma}^2$$
$$+[-\mu_3\cos\gamma+\rho\mu_3^2r_1r_2\sin^2\gamma]\dot{r}_1\dot{r}_2+\rho\mu_3r_1r_2\sin\gamma\{[\mu_1r_1-\mu_3r_2\cos\gamma]\dot{r}_1\dot{\gamma}+[\mu_2r_2-\mu_3r_1\cos\gamma]\dot{r}_2\dot{\gamma}\}$$
$$-\tfrac{1}{2}[k_1(\Delta r_1)^2+k_2(\Delta r_2)^2+k_3(r_1^{0^2}+r_2^{0^2})(\Delta\gamma)^2], \tag{6}$$

in which $1/\rho=\mu_1r_1^2+\mu_2r_2^2-2\mu_3r_1r_2\cos\gamma$.

Since the vibrations are small, the equilibrium values r_1^0, r_2^0, γ^0 of r_1, r_2, γ, respectively, may be substituted in the coefficients of the velocity terms in (6). Then if we introduce new coordinates $q_1=\Delta r_1$, $q_2=\Delta r_2$, $q_3=(r_1^{0^2}+r_2^{0^2})^{\frac{1}{2}}\Delta\gamma$, we have

$$R=\tfrac{1}{2}\sum_i\sum_j a_{ij}\dot{q}_i\dot{q}_j-\tfrac{1}{2}\sum_i k_iq_i^2,\quad (a_{ij}=a_{ji}). \tag{7}$$

The values of the constants a_{ij} are immediately obtained from Eq. (6). The three equations of motion obtained from the Lagrangian function (7) are

$$a_{i1}\ddot{q}_1+a_{i2}\ddot{q}_2+a_{i3}\ddot{q}_3+k_iq_i=0,\quad (i=1,2,3). \tag{8}$$

[10] Cf., for instance, Whittaker, *Analytical Dynamics*, Third edition, page 54, Cambridge, 1927.

The usual assumption of a periodic solution $q_i=A_ie^{-i\lambda t}$ yields the following relations for determination of the amplitudes.

$$[a_{i1}A_1+a_{i2}A_2+a_{i3}A_3]\lambda^2-k_iA_i=0,\ (i=1,2,3). \tag{9}$$

The existence of a non-trivial solution of the three Eqs. (9) requires that the determinant of the coefficients vanish, whence

$$\begin{vmatrix} a_{11}\lambda^2-k_1 & a_{12}\lambda^2 & a_{13}\lambda^2 \\ a_{21}\lambda^2 & a_{22}\lambda^2-k_2 & a_{23}\lambda^2 \\ a_{31}\lambda^2 & a_{32}\lambda^2 & a_{33}\lambda^2-k_3 \end{vmatrix}=0. \tag{10}$$

From this equation the constants necessary to yield solutions of the Eqs. (9) may be determined.

III. Evaluation of the Force Constants

The interatomic distances given in Table I were calculated from the values of the atomic radii given by Sigwick and Bowen.[11] The carbon to carbon distance r_2^0 was taken throughout as 1.54A. No experimental values of the angles between the valence directions were available, but as shown in Section I, they cannot vary greatly from the tetrahedral angle.

Values of the force constants, k_1, k_2 and k_3, were determined which made the roots of (10) equal to the experimental values of λ^2, which have the significance $\lambda^2=4\pi^2c^2\omega^2$ in terms of the wave number ω.[12] In case no reasonable real values of the force constants would give the required roots of (10), values were selected which gave roots nearly the same as those obtained from experimental data. Values of these constants, together with the calculated values of ω and the wave numbers of the corresponding Raman lines, are given in Table I.

Table I.

	r_1^0(A)	$k_1\times10^{-5}$	$k_2\times10^{-5}$	$k_3\times10^{-5}$	ω_1(cm^{-1}) Calc.	Obs.	ω_2(cm^{-1}) Calc.	Obs.	ω_3(cm^{-1}) Calc.	Obs.
CH_3CH_2Cl	1.74	2.2	3.9	0.22	660	655	980	966	335	335
CH_3CH_2Br	1.9	1.6	3.8	0.22	570	560	970	960	285	290
CH_3CH_2I	2.1	1.2	3.8	0.18	510	500	960	950	245	260
CH_3CH_2OH	1.37	4.1	3.6	0.26	910	885	1020	1045	430	425

As an alternative the force constants of the potential function (1) were calculated, and are as follows:

CH_3CH_2Cl; $c_{13}=2.5\times10^5$, $c_{23}=3.8\times10^5$, $c_{12}=1.2\times10^5$.

CH_3CH_2Br; $c_{13}=2.25\times10^5$, $c_{23}=3.75\times10^5$, $c_{12}=1.0\times10^5$.

CH_3CH_2I; $c_{13}=1.96\times10^5$, $c_{23}=3.7\times10^5$, $c_{12}=0.78\times10^5$.

CH_3CH_2OH; $c_{13}=4.0\times10^5$, $c_{23}=3.5\times10^5$, $c_{12}=1.7\times10^5$.[13]

Insofar as the consistency of the values of the force constants is concerned, there is little basis for a choice between the two potential functions. In particular, the value of k_2 or c_{23} should not vary greatly from molecule to molecule since the the intensity of the CH_3-CH_2 bond should be but little affected by the nature of the other atom attached to the C atom. This condition is seen to be met with either the potential function (2) based on valence forces, or with the less likely alternative (1).

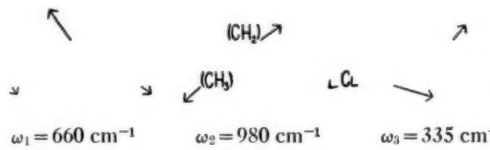
IV. The Normal Modes of Vibration

After determination of the force constants, k_i, the roots of Eq. (10) were substituted in (9) to obtain the ratio $A_1:A_2:A_3$ for each frequency. The corresponding values of A_ϕ were obtained from the relation $\partial L/\partial\dot{\phi}=P=0$. The resulting normal modes of vibration are shown in Figs. 3 to 6.

[11] N. V. Sidgwick and E. J. Bowen, Ann. Rep. Chem. Soc. **28**, 402 (1931).

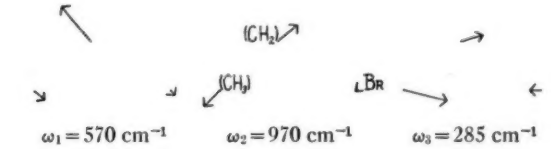
[12] Eq. (10) is a cubic, $\lambda^6+\alpha\lambda^4+\beta\lambda^2+\gamma=0$, in λ^2. In the evaluation of its roots λ_1^2, λ_2^2, λ_3^2, it is convenient to utilize the well-known expressions $\gamma=-\lambda_1^2-\lambda_2^2-\lambda_3^2$, $\beta=\lambda_1^2\lambda_2^2+\lambda_1^2\lambda_3^2+\lambda_2^2\lambda_3^2$, $\alpha=-\lambda_1^2\lambda_2^2\lambda_3^2$. Explicit formulas for α, β and γ in terms of the masses, force constants and molecular dimensions have been given by Lechner[9] and so need not be repeated here. Lechner expresses the equations of motion in the form $\ddot{q}_i=\Sigma a_{ij}q_j$ rather than (8), but we have verified that his secular equation is the same as ours.

[13] There are no real values of c_i, which give the experimental values of ω for ethyl alcohol. The values given here correspond roughly to values 1015, 935 and 425 cm^{-1} for ω.



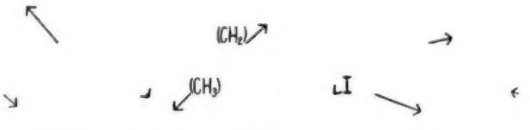
$\omega_1 = 660$ cm^{-1} $\omega_2 = 980$ cm^{-1} $\omega_3 = 335$ cm^{-1}

FIG. 3.



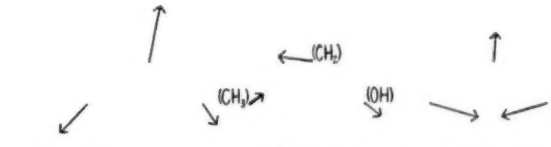
$\omega_1 = 570$ cm^{-1} $\omega_2 = 970$ cm^{-1} $\omega_3 = 285$ cm^{-1}

FIG. 4.



$\omega_1 = 510$ cm^{-1} $\omega_2 = 960$ cm^{-1} $\omega_3 = 245$ cm^{-1}

FIG. 5.



$\omega_1 = 910$ cm^{-1} $\omega_2 = 1020$ cm^{-1} $\omega_3 = 430$ cm^{-1}

FIG. 6.

V. The Effect of Cross Terms in the Potential Function

We shall now consider briefly the effect of adding the cross-terms

$$\tfrac{1}{2}\sum_i\sum_{j(j\neq i)}k_{ij}q_iq_j \quad (k_{ij}=k_{ji}) \tag{11}$$

to the potential function of (7). The existence and origin of these terms was discussed in Section I. The addition of (11) merely introduces into the equations of motion (8) the extra term $\sum_j k_{ij}q_j$. The resulting secular equation is still a cubic, but as it can be solved only numerically, the addition of (11) introduces so many arbitrary constants that the problem ceases to be tractable or significant. Instead, the extent to which (11) influences the frequencies can be more easily studied if one introduces it as a perturbation. The result of the perturbation is perhaps best examined by introducing normal coordinates, $A_1\cdots$, for the unperturbed problem. The coordinates q_1, q_2, q_3 will be linear functions $q_i=\sum_j\alpha_{ij}A_j$ of these coordinates. After addition of (11) these coordinates lose their "normal" property and the Lagrangian function in terms of the A's may be thrown into the form:

$$R'=\tfrac{1}{2}\sum_j[A_j^2-\lambda_j^2A_j^2]-\tfrac{1}{2}\sum_i\sum_j\beta_{ij}^2A_iA_j, \tag{12}$$

with

$$\beta_{ij}=\beta_{ji}=\sum_l\sum_{m(l<m)}k_{lm}(\alpha_{li}\alpha_{mj}+\alpha_{lj}\alpha_{mi}).$$

The secular equation is then

$$\begin{vmatrix}\beta_{11}+\lambda_1^2-\lambda'^2 & \beta_{12} & \beta_{13}\\ \beta_{21} & \beta_{22}+\lambda_2^2-\lambda'^2 & \beta_{23}\\ \beta_{31} & \beta_{32} & \beta_{33}+\lambda_3^2-\lambda'^2\end{vmatrix}=0. \tag{13}$$

Here primes are attached to the λ's when we wish to designate their values as modified by the inclusion of (11). The approximate solution of (13) is

$$\lambda_i'^2=\lambda_i^2+\beta_{ii}-\sum_{j(j\neq i)}\beta_{ij}^2/(\lambda_j^2-\lambda_i^2) \tag{14}$$

if the off-diagonal elements of (13) are small in comparison with the differences $\lambda_j^2-\lambda_i^2$.

The effect of the introduction of the cross-terms may best be examined by writing down a specific numerical form of (14) for a particular example, ethyl alcohol.

$$\begin{aligned}\lambda_1'^2-\lambda_1^2&=(0.6k_{12}-1.17k_{13}-1.85k_{23})\times10^{23}\\&\quad-(0.06k_{12}^2+1.15k_{13}^2+0.47k_{23}^2-0.62k_{12}k_{13}+0.35k_{12}k_{23}-2.34k_{13}k_{23})\times10^{18}.\\ \lambda_2'^2-\lambda_2^2&=(-0.94k_{12}-0.1k_{13}+0.08k_{23})\times10^{23}\\&\quad+(0.06k_{12}^2+1.65k_{13}^2+1.06k_{23}^2-0.54k_{12}k_{13}+0.41k_{12}k_{23}-2.64k_{13}k_{23})\times10^{18}.\\ \lambda_3'^2-\lambda_3^2&=(0.03k_{12}+0.31k_{13}+0.37k_{23})\times10^{23}\\&\quad-(0.01k_{12}^2+0.47k_{13}^2+0.64k_{23}^2+0.08k_{12}k_{13}+0.08k_{12}k_{23}-0.3k_{13}k_{23})\times10^{18}.\end{aligned} \tag{15}$$

A rough estimate of the k_{ij}'s by a procedure similar to that used in evaluating $g(r_{12})$ in the following paper yields the values $k_{12}=0.13\times10^5$, $k_{13}=0.039\times10^5$, $k_{23}=0.044\times10^5$. Introduction of these terms gives the values $\lambda_1'^2=2.9\times10^{28}$, $\lambda_2'^2=3.58\times10^{28}$, $\lambda_3'^2=0.685\times10^{28}$ for the perturbed frequencies. The unperturbed values are $\lambda_1^2=2.95\times10^{28}$, $\lambda_2^2=3.7\times10^{28}$, $\lambda_3^2=0.655\times10^{28}$. These values could be altered by choosing other values for the constants k_1, k_2, k_3 in the unperturbed system, but it appears unlikely that the separation of λ_1^2 and λ_2^2 could be made great enough to agree with the experimental data. The separation is probably partly due to certain factors that have been neglected, such as the effect of the hydrogen atoms on the potential function and on the effective masses of the units, or to errors in the dimensions of the molecules. Despite this discrepancy, however, the approximate validity of the calculations is retained.

VI. Conclusion

It is apparent from the normal modes of vibration of the systems studied that the designation of a type of motion involving only a part of the molecule to account for certain frequencies is justified under certain conditions of dissymmetry. This may in a large measure be responsible for the well-established fact that certain chemical bonds are accompanied by frequencies which vary but little from a mean value as drastic changes are made in other parts of the molecule. However, as was suggested by Cross and Daniels, the presence of certain types of symmetry, such as the approximate mass symmetry of ethyl alcohol, may cause an interaction of the different types of motion in such a way as to largely obliterate the characteristic features of the separate types of motion.

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A Calculation of the Vibration Frequencies and Other Constants of the H_2O Molecule

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The calculation is based on the Slater-Pauling theory of directed valence, but supplemented by data from the band spectrum of the diatomic OH molecule. The heat of dissociation and valence angle, obtained incidentally, are in good agreement with experiment. The "cross-terms" in the vibrational potential prove to be of subordinate importance. It is found that two of the fundamentals should fall near 2.8μ, and that they should almost coincide. This designation of the observed wide absorption band at 2.6–2.8μ as the superposition of two fundamentals agrees with Mecke's interpretation of the H_2O spectrum, but contradicts Johnston and Walker's. The computed value 1660 cm^{-1} of the third fundamental frequency ω_3 differs from experimental determinations by only 4 percent, but any closer agreement than 15 percent is accidental in view of the approximate nature of the theory. Since ω_3 represents a primarily angular vibration, its calculation is a particular test of the concepts of directed valence.

THE water molecule is of interest because it is possible to calculate its vibration frequencies and other constants by a method based on quantum mechanics supplemented by spectroscopic data from the OH and H_2 (but not the H_2O) molecules. This process should not be confused with the less exacting, more customary procedure, used in the preceding paper, of simply adjusting force constants to yield agreement with observed vibration bands. Our calculation of the fundamental frequencies will, of course, include a theoretical evaluation of the coefficients in the vibrational potential,

$$V=\tfrac{1}{2}[k_1(\Delta r_1)^2+k_2(\Delta r_2)^2+2k_3{r_1}^{0^2}(\Delta\gamma)^2] +k_{12}\Delta r_1\Delta r_2+2^{\frac{1}{2}}k_{13}{r_1}^0(\Delta r_1\Delta\gamma+\Delta r_2\Delta\gamma), \quad (1)$$

where r_1, r_2 are the O−H separations, and γ is the angle H−O−H (cf. Fig. 2 of reference 1). The factors ${r_1}^{0^2}$, ${r_1}^0$ are inserted, as in reference 1, to secure dimensional similarity in the k's. It turns out that the coefficients k_{12} and k_{13} are relatively unimportant. This fact furnishes at least partial justification for treatment of the "cross-terms" in the potential as small perturbations, as in the preceding paper on the ethyl halides,[1] or even the complete omission of these terms, as in the hypothesis of "valence forces" often made in the literature.

According to the quantum theory of directed valence, the potential energy of an H_2O molecule should be approximately of the form

$$V=f(r_1)+f(r_2)+g(r_{12}) +3(N_{\sigma\sigma}-N_{\pi\pi})\sin^2(\tfrac{1}{2}\gamma-\tfrac{1}{4}\pi). \quad (2)$$

Here $N_{\sigma\sigma}$ and $N_{\pi\pi}$ are, except for sign, exchange integrals between a $1s$ state of H and respectively the $2p\sigma$ and $2p\pi$ states of O, space quantized relative to the corresponding O−H axis.[2] The terms $f(r_1)$, $f(r_2)$ in (2) are radial O−H potentials, and, to our approximation, are of the same functional form as the potential energy curve for the diatomic OH molecule. The term $g(r_{12})$ represents the repulsion between the two H atoms, whose separation is denoted by r_{12}. The remaining term gives the effect of directional valence, and proves to be considerably more important than $g(r_{12})$. That this term has the form of dependence on γ given in (2) follows from the Slater-Pauling theory of directed valence provided one makes the hypothesis of electron pairing.[3]

[1] P. C. Cross and J. H. Van Vleck, J. Chem. Phys. **1**, 350 (1933). See this reference for more general discussion of molecular vibrations.

[2] The notation is chosen in conformity with that used by one of us in J. Chem. Phys. **1**, 219 (1933). The reader is referred especially to Sections 5 and 6 of this reference if he desires further information concerning the concepts of the quantum mechanics of directed valence, electron pairing, etc. which we are using. Note especially that our N's are the negative of exchange integrals.

[3] The angular term of (2) is essentially the same as that given by Slater in Phys. Rev. **38**, 1139 (1931), except that

Details of the derivation of the last term of (2) are as follows: Let us take the O nucleus as the origin and suppose that the H nuclei lie in the xy plane. Let us further take the bisector of the angle H−O−H to be inclined at 45° to the x axis. Then

$$\cos(r_1, x) = \cos(r_2, y) = \cos(\tfrac{1}{2}\gamma - \tfrac{1}{4}\pi). \quad (3)$$

The configuration of the O atom may, with this choice of axes, be taken[4] to be $1s^2 2s^2 2p\sigma_z^2 2p\sigma_x 2p\sigma_y$. Here $2p\sigma_z$, for instance, denotes a $2p$ wave function having $m_l = 0$ when space quantized relative to the z axis. From the rotational transformation properties of $2p$ wave functions, it follows[5] that the exchange integral J_{1x} connecting the $1s$ wave function of H atom 1 and the $2p\sigma_x$ wave function of O is

$$J_{1x} = -N_{\sigma\sigma}\cos^2(r_1, x) - N_{\pi\pi}\sin^2(r_1, x) = J_{2y}. \quad (4)$$

Similarly

$$J_{1z} = J_{2z} = -N_{\pi\pi}, \quad (5)$$

$$J_{2x} = J_{1y} = -N_{\sigma\sigma}\sin^2(r_1, x) - N_{\pi\pi}\cos^2(r_1, x). \quad (6)$$

We shall let J denote the sum of the exchange integrals for the pairs ($1s$ of H; $1s$ of O) and ($1s$ of H; $2s$ of O). Clearly J has the same value for either H atom and is independent of γ. If we make the hypothesis of electron pairing the exchange energy is[6]

$$J_{1x} + J_{2y} - \tfrac{1}{2}J_{2x} - \tfrac{1}{2}J_{1y} + 2(-\tfrac{1}{2}J_{1z} - \tfrac{1}{2}J_{2z} - J). \quad (7)$$

The terms with coefficients $+1$ in (7) are those which represent pairs. When one expresses the exchange integrals involved in (7) in terms of $N_{\sigma\sigma}$, $N_{\pi\pi}$, γ with the aid of (3–6), one obtains the last term of (2) except for an additive constant $-2J - 2N_{\sigma\sigma} + 3N_{\pi\pi}$. This constant must not be inserted in (2), since it is included in $f(r_1) + f(r_2)$. Namely, the binding energy for OH is

$$f(r_1) = -J - N_{\sigma\sigma} + \tfrac{3}{2}N_{\pi\pi} + \text{polar and Coulomb terms}, \quad (8)$$

so that $f(r_1) + f(r_2)$ absorbs all of the exchange energy at $\gamma = \frac{1}{2}\pi$. Eq. (8) is proved from (7) by dropping all terms which involve atom 2, and keeping atom 1 on the x axis. The polar and Coulomb terms are to be added in (8) since (7) aims to give only the exchange energy. We have tacitly assumed that the polar and Coulomb effects do not depend on direction. This appears to be an allowable approximation.

It must be cautioned that in the foregoing, we have assumed that the O atom always remains in the configuration s^2p^4, or in other words that there is no $s-p$ hybridization for this atom. Any amount of this hybridization tends to intensify the bonds, but the $s-p$ separation of the O atom amounts to over 15 volts, and so the O atom is probably unwilling to make a partial change from s^2p^4 towards sp^5 in order to hold the H atoms tighter. On the other hand, hybridization apparently must be considered in connection with the molecular vibrations of NH_3, as otherwise it seems impossible to explain the low potential hill[7] ($\frac{1}{4}$ volt) involved in converting one isomer of NH_3 into the other. This difference between H_2O and NH_3 does not appear unreasonable, since the $s-p$ separation is smaller (11 volts) in N than in O and since hybridization is a greater advantage with 3 than with 2 bonds.

We shall assume that $f(r_1)$, $f(r_2)$ and $g(r_{12})$ can be represented by Morse functions. This procedure has been at least partially justified by the success of Eyring's[8] well-known investigations of activation. The values of $f(r_1)$ and $g(r_{12})$ can then be determined from the potential energy curves yielded by the band spectra of OH and H_2 and are as follows[9]

$$f(r_1) = 120(1 - e^{2.15(0.98 - r_1)})^2 - 120,$$

$$g(r_{12}) = -35(1 - e^{1.85(0.75 - r_{12})})^2 + 35.$$

Here distances are supposed measured in Angstroms, and the amplitudes have been in terms of a kg·cal./g·mol scale of energy. In evaluating

he has introduced explicit numerical values of the N's. In fact our calculation of the equilibrium position and energy is very similar to that given by Slater except that we use different, and we believe better, numerical constants. Our equilibrium calculations are intended primarily as prerequisites to the vibrational analysis, which was not considered by Slater.

[4] By the methods of reference 2 one can show that any other, less symmetrical, choice of spatial quantization for the $2p$ wave functions of oxygen will yield a higher value of the energy if the hypothesis of electron pairing is made.

[5] See Eq. (6) of reference 2 and related discussion.

[6] Cf. Eq. (35) of reference 2.

[7] D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41** 313 (1932); N. Rosen and P. Morse, ibid. **42**, 211 (1933).

[8] H. Eyring and M. Polanyi, Zeits. f. physik. Chemie **12**, 279 (1931); H. Eyring, J. Am. Chem. Soc. **53**, 2537 (1931); Sherman and Eyring, ibid. **54**, 2661 (1932).

[9] Our choice of Morse functions has been determined to fit the vibration frequency and the heat of dissociation rather than the former and the anharmonic correction. For the band spectrum data see Weizel, *Bandspektren*, or Mulliken, Rev. Mod. Phys. **4**, 1 (1933). In our formula for $g(r_{12})$ we have not attempted to make allowance for the fact that the polar character of H_2O makes the H atoms each have an excess of positive over negative charge and so exert ionic repulsive forces upon each other. This repulsion is perhaps roughly counterbalanced by the van der Waals force between the H atoms, not included at large separations in the Morse function. Both the ionic and van der Waals forces are probably subordinate to those covered by the Morse function. The van der Waals term is hard to estimate accurately, as Eyring notes (J. Am. Chem. Soc. **54**, 3201 (1932)) that the inverse sixth power polarization potential gives excessive values at distances as small as r_{12}. In this reference he compares qualitatively the forces resulting from directional valence and H−H repulsions in H_2O, and notes that the latter are, as we find, not entirely negligible compared with the former.

$g(r_{12})$, we have, like Eyring, supposed that the binding energy of an H_2 molecule is 10 percent Coulomb, and 90 percent exchange. This makes $g(r_{12})$ 35 percent of a Morse function for H_2, inasmuch as exchange terms connecting electrons involved in different pairs involve the coefficient $-\frac{1}{2}$ rather than $+1$, making[8] the proportionality factor $0.1-(\frac{1}{2}\times 0.9)=-0.35$. On the other hand $f(r_1)$ and $f(r_2)$ are complete Morse functions for OH.

The values of $N_{\sigma\sigma}$ and $N_{\pi\pi}$ will be taken as 2 and -0.6 volt, respectively. These estimates have been obtained largely from the potential curves of the OH molecule, and are perhaps accurate to 20 percent or so. The details of the method of estimation will be published in a future paper by J. R. Stehn and J. H. Van Vleck. Incidentally, the agreement with the values 2.3 and -0.6 volts obtained by Coolidge[10] by actual computation of the integrals with Zener's wave functions is gratifying. We believe the spectroscopic method to be perhaps more reliable than the computational one. As a matter of fact, the spectroscopic method gives a value of $N_{\sigma\sigma}$ somewhat below 2 volts, but we have used the round value 2 in order to give some weight to Coolidge's calculations. With our estimate of the N's, one has

$$3(N_{\sigma\sigma}-N_{\pi\pi})=180 \text{ kg}\cdot\text{cal./g}\cdot\text{mol.}$$

One must now make a Taylor's development of (2) about the equilibrium position r_1^0, r_2^0, γ^0. Inasmuch as $r_{12}^2=r_1^2+r_2^2-2r_1r_2\cos\gamma$ and $r_1^0=r_2^0$ this development is

$$\begin{aligned}V=V(r_1^0,\,r_2^0,\,\gamma^0,\,r_{12}^0)&+\left(\frac{\partial f}{\partial r_1}\right)^0(\Delta r_1+\Delta r_2)-\tfrac{3}{2}(N_{\sigma\sigma}-N_{\pi\pi})\cos\gamma^0\cdot\Delta\gamma\\&+\left(\frac{\partial g}{\partial r_{12}}\right)^0[\sin\tfrac{1}{2}\gamma^0\cdot(\Delta r_1+\Delta r_2)+r_1^0\cos\tfrac{1}{2}\gamma^0\cdot\Delta\gamma]+\tfrac{1}{2}\left(\frac{\partial^2 f}{\partial r_1^2}\right)^0[(\Delta r_1)^2+(\Delta r_2)^2]\\&+\tfrac{3}{4}(N_{\sigma\sigma}-N_{\pi\pi})\sin\gamma^0\cdot(\Delta\gamma)^2+\tfrac{1}{2}\left(\frac{\partial^2 g}{\partial r_{12}^2}\right)^0[\sin\tfrac{1}{2}\gamma^0\cdot(\Delta r_1+\Delta r_2)+r_1^0\cos\tfrac{1}{2}\gamma^0\cdot\Delta\gamma]^2\\&+\left(\frac{\partial g}{\partial r_{12}}\right)^0\left[\frac{\sin^2\gamma^0}{16r_1^0\sin^3\frac{1}{2}\gamma^0}(\Delta r_1-\Delta r_2)^2+\tfrac{1}{2}\cos\tfrac{1}{2}\gamma^0(\Delta r_1\Delta\gamma+\Delta r_2\Delta\gamma)-\tfrac{1}{4}r_1^0\sin\tfrac{1}{2}\gamma^0\cdot(\Delta\gamma)^2\right].\end{aligned}\tag{9}$$

The values of r_1^0, r_2^0 and γ^0 are respectively determined by the requirement that the coefficients of Δr_1, Δr_2 and $\Delta\gamma$ vanish in (9). This gives

$$r_1^0=r_2^0=1.00 \text{ Angstrom},\quad \gamma^0=100°.\tag{10}$$

This value of r^0 agrees with the fact that the experimental determinations are practically the same as the equilibrium distance 0.98 Angstrom in the diatomic OH molecule. The value of γ^0 is in sufficient accord with the various estimates of from 102° to 111° which have been obtained from band spectra.[11] The heat of dissociation into 2H+O is $V(r_1^0,\,r_2^0,\,\gamma^0,\,r_{12}^0)$, or 205 kg·cal./mol. Expressed in volts, this estimate is 8.9 volts. Thermochemical data lead to a value of about 10 volts.[12] Our theoretical estimate is

[10] A. S. Coolidge, Phys. Rev. **42**, 189 (1932).

[11] For instance, Eucken finds $\gamma^0=110°\ 56'$ while Mecke obtains a value between 102° and 111°.

[12] The good agreement of the calculated and observed heats of dissociation should not be considered any particular triumph, for any theory based on electron pairing will predict approximately twice as great a heat of dissociation for H_2O as for OH. (Cf. J. H. Van Vleck, J. Chem. Phys. **1**, 177 (1933). If we assume electron pairing, it is not necessary to neglect interaction between the H atom and the $2s$ or $2p\pi$ states of O, as there stated, in order to obtain the factor 2.) For instance, Slater[3] secures equally good agreement with entirely different assumed values of the exchange integrals. On the other hand, the calculation of the transverse vibration frequency ω_3 is sensitive to the evaluation of these integrals. Our semi-quantum mechanical, semi-spectroscopic calculation of the heat of dissociation should not be confused with Coolidge's purely quantum mechanical treatment, which led to the excessively low value -5.7 volts. The writers believe that two reasons why Coolidge obtained too low a result may be the following: (a) He assumed the same exponential factor for the carbon $2s$ and $2p$ wave functions, whereas actually

raised to 9.4 when correction[13] is made for the L, S structure of the O configuration s^2p^4.

By substitution of (10) in (9), we find that the coefficients in (1) have the following numerical values:

$$k_1=k_2=6.96\times10^5, \quad k_3=0.379\times10^5,$$
$$k_{12}=0.165\times10^5, \quad k_{13}=0.04\times10^5.$$

The values of the constants involved in (7) of our preceding paper are

$$a_{11}=a_{22}=15.6\times10^{-25}, \quad a_{33}=3.86\times10^{-25},$$
$$a_{12}=0.185\times10^{-25}, \quad a_{13}=a_{23}=0.32\times10^{-25}.$$

Because of the addition of the cross-terms, the simultaneous equations (8) of the preceding article for determining the molecular vibrations are to be enhanced by the term $\sum_j k_{ij}q_j$, with corresponding modification of the cubic secular equation (10) of the foregoing paper. In virtue of the symmetry of the molecule, this cubic factors into a linear and a quadratic equation in $\lambda^2=4\pi^2c^2\omega^2$; as follows:

$$(a_{11}-a_{12})\lambda^2-k_1+k_{12}=0,$$
$$[(a_{11}+a_{12})\lambda^2-k_1-k_{12}][a_{33}\lambda^2-k_3] -2[a_{13}\lambda^2-k_{13}]^2=0. \quad (11)$$

Substitution of numerical values yields

$$\omega_1=3520\,\text{cm}^{-1}, \omega_2=3560\,\text{cm}^{-1}, \omega_3=1660\,\text{cm}^{-1}. \quad (12)$$

Experimentally regions of intense absorption occurs at 1600 and 3700 cm^{-1}.[14] It is not at all surprising that the calculated radial vibrations come near 3600 cm^{-1} for this is merely because the primarily radial vibrations have nearly the same frequency as that characteristic of OH. Conclusions of more interest are the following:

(1) The coefficients k_{12}, k_{13} in (1) are comparatively small, so that inclusion of the "cross-terms" does not greatly modify the calculated frequencies. In fact, if one sets $k_{12}=k_{13}=0$, the computed frequencies become 3560, 3520, 1660 cm^{-1} instead of (12). The frequencies ω_1 and ω_2 have the significance of being associated with unsymmetrical and symmetrical primarily radial vibrations: i.e., ω_1 has $\Delta r_1=-\Delta r_2$, $\Delta\gamma=0$ while ω_2, like ω_3, has $\Delta r_1=\Delta r_2$.

(2) The difference $\lambda_1^2-\lambda_2^2$ is given approximately by the equation

$$\lambda_1^2-\lambda_2^2=\frac{2(-a_{11}k_{12}+a_{12}k_1)}{a_{11}^2-a_{12}^2} -\frac{2[a_{13}^2(k_1+k_{12})-a_{13}k_{13}(a_{11}+a_{12})]}{a_{33}(a_{11}+a_{12})^2}. \quad (13)$$

The second term is quite small in the case of water, contributing only about 10 percent of the total separation. It is interesting to note that the contribution of the k_{12} term is about twice as large as that of the a_{12} term, and is of the opposite sign. The value of a_{12} is the following function of γ^0:

$$a_{12}=-\mu_3\cos\gamma^0+\frac{\mu_3^2\sin^2\gamma^0}{2(\mu-\mu_3\cos\gamma^0)}, \quad (\mu=\mu_1=\mu_2). \quad (14)$$

The second term of (14) is about $\frac{1}{6}$ as large as the first one. Attempts have been made in the literature to calculate γ^0 for H_2O from the experimental values of λ_1^2 and λ_2^2 by means of the relation

$$\cos\gamma^0=-\frac{M_H+M_O}{M_H}\cdot\frac{\lambda_1^2-\lambda_2^2}{\lambda_1^2+\lambda_2^2} \quad (15)$$

obtained by setting $a_{12}=-\mu_3\cos\gamma^0$ and $a_{13}=a_{23}=k_{12}=k_{13}=0$ in Eq. (11). It is obvious that such a method of obtaining the equilibrium angle is not reliable since small values of the cross-

the $2s$ states are more firmly held and so have a larger negative exponent. This implies that Coolidge overestimated the exchange repulsion from the $2s$ states. (b) Examination of potential curves for OH suggests that the ionic attraction per atom is somewhat larger than his estimate of 1.1 volts. Coolidge's difficult and noteworthy calculation goes to the refinement of considering more than simple permutations. The results of his paper suggest that possibly the first order Heitler-London calculation is somehow a better approximation without than with allowance for the higher order permutations.

[13] Under the hypothesis of electron pairing the valence state of H_2O may be shown to be $\frac{3}{4}\,{}^3P+\frac{1}{4}\,{}^1D$. The fractional coefficients occur because the pairing prevents L, S of O from being good quantum numbers. When we double the Morse function for OH we allow the O atom twice the activation energy necessary to raise it from ^3P to the valence state. Actually the activation energy of O is the same for OH as for H_2O, so that our estimate of the heat of dissociation should be increased by one quarter of the interval $^1D-{}^3P$, or by 0.5 volt.

[14] W. W. Sleator, Astrophys. J. **48**, 125 (1918).

terms k_{12} will completely alter the character of the right side of (13).[15]

(3) The difference $\omega_1-\omega_2$ is so small that it is comparable with the rotational structure. Hence it is not surprising that the frequencies ω_1, ω_2 have not yet been resolved experimentally. Actually, the band at 3700 cm^{-1} is extremely diffuse. Johnston and Walker[16] claim to have located ω_2 at 984 cm^{-1} from the Raman effect, but such a value of ω_2 is entirely out of the question unless the theory is devoid of all meaning. Our interpretation of the band as a superposition of ω_1, ω_2 is similar to that proposed by Mecke.[17, 18]

(4) The HOH^2 molecule, involving the isotope H^2, may be assumed to have the same potential function as the HOH molecule. If the force constants k_1, k_3 are adjusted to give absorption regions at approximately 3750 cm^{-1} for ω_1 and ω_2 and at 1600 cm^{-1} for ω_3 of the HOH molecule, the fundamental bands of HOH^2 should occur at 3750, 2720, and 1400 cm^{-1}.

(5) The agreement between the calculated and observed values of ω_3 is particularly gratifying, for ω_3 represents an angular mode of vibration not found in OH, and originates in the resistance of directional valence to any bending of the molecule from the equilibrium angle. It must be remembered that the calculations, from their very nature, do not claim any great precision, and agreement only to within 15 percent[19] or so would not have been disconcerting. The calculations on ω_3 thus confirm the essential correctness of the Slater-Pauling concept of directed valence.

[15] In molecules where the central atom is not of large mass compared to the attached ones, the difference $\lambda_1^2-\lambda_2^2$ is not small, and must be calculated from the exact formulas (11) rather than from the approximate relation (13). When the central atom and attached masses are comparable, as in the examples studied by Lechner, (Monats. f. Chem. **61**, 395 (1932)) the terms involving a_{12} overshadow those proportional to k_{12} and k_{13}. Hence Lechner's calculation of equilibrium angles would not be materially modified by inclusion of cross-terms in the potential.

[16] H. L. Johnston and M. K. Walker, Phys. Rev. **39**, 535 (1932). Our ω_1, ω_2, ω_3 correspond to Johnston and Walker's Dennison's) ν_3, ν_1, ν_2, respectively.

[17] R. Mecke. Zeits. f. physik. Chemie **16**, 431 (1932).

[18] *Note added in proof:* Papers by Mecke, Baumann and Freudenberg (Zeits. f. Physik **81**, 313, 445, 465 (1933)) have just appeared which give a very careful analysis of the rotation-vibration bands of water. They find ω_1 and ω_2 at 3756 and 3600 cm^{-1}, respectively. Thus $\omega_2-\omega_1$, according to their analysis, has a different sign and larger numerical magnitude than in our theoretical estimate $\omega_2-\omega_1=40$ cm^{-1}. This, however, need not cause concern, since $\omega_2-\omega_1$ is still small, in qualitative accord with theory, and quantitative accuracy in the theoretical calculation of a difference as small as $\omega_2-\omega_1$ is not to be expected in view of the many approximations which it is necessary to make, notably the assumption of electron pairing. Also, the experimental determination of ω_2 is not free from difficulty, and Mecke mentions that the region from 3300 to 3600 cm^{-1} has so far defied exact analysis. An interesting problem is presented by the fact that Mecke finds ω_2 to be an inactive frequency except when involved in combinations with ω_1. If one assumes that the motions of the water molecule can be represented by the vibrations of a system of three particles, each with a constant charge, then one must expect ω_2 to be an active frequency. However, it is probable that the water molecule becomes increasingly ionic in character when r_{13} and r_{23} are simultaneously diminished. If so, migrations of charge back and forth between the O and H atoms accompany the vibrations. It is thus conceivable that equal displacements in r_{13} and r_{23} at nearly constant γ may give rise to little change in moment, due to a cancellation of the change due to migration and the change calculated for a model in which the atoms have constant charges. In this fashion ω_2 might be inactive.

[19] The error in ω_3 can be less than in the exchange integrals because ω_3 is roughly proportional to $(N_{\sigma\sigma}-N_{\pi\pi})^{\frac{1}{2}}$.

The Nature of the Chemical Bond. V. The Quantum-Mechanical Calculation of the Resonance Energy of Benzene and Naphthalene and the Hydrocarbon Free Radicals[1]

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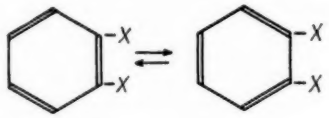
The secular equations corresponding to the five canonical structures for benzene and the forty-two for naphthalene, considered as six and ten-electron systems, respectively, are set up and solved with certain simplifying assumptions, leading to energy values differing by 1.1055α and 2.0153α, respectively, from those corresponding to unexcited (Kekulé-type) structures, α being a single exchange integral involving neighboring carbon atoms. Equating these values to the empirical values of the resonance energy, α is found to be about -1.5 v.e.

It is pointed out that the dissociation of certain substituted ethanes into free radicals is due not to weakness of the carbon-carbon bond in the ethane but to the stabilization of the free radicals resulting from resonance among the structures in which the unpaired electron is located on the methyl carbon and those in which it is on other atoms (ortho, para, etc., to the methyl carbon). The secular equations for a number of such radicals have been solved, neglecting excited structures. The experimentally determined heat of formation of hexaphenylethane from triphenylmethyl, 0.5 v.e., when equated to the calculated value $C-C+2.2156\alpha$, with $C-C=3.65$ v.e., leads to $\alpha=-1.4$ v.e. The calculated tendencies towards dissociation are in satisfactory agreement with observation, such features as the smaller dissociating power of β-naphthyl than of α-naphthyl and of biphenylene than of diphenyl being accounted for, so that resonance among the structures considered may be accepted as the principal effect causing the stability of the hydrocarbon free radicals.

THE STRUCTURE OF BENZENE AND NAPHTHALENE

A NUMBER of structural formulae have been proposed for benzene, but none of them is free from very serious objections.

The oldest and best known structure is that proposed by Kekulé (I). The objections to it are twofold. First, it suggests that ortho-disubstituted derivatives should exist in two isomeric forms—a phenomenon which has never been observed. Kekulé avoided this difficulty, however, by assuming that the double bonds were in a state of constant oscillation such that any two adjacent carbon atoms were connected part of the time by a single bond and part of the time by a double bond. For example:



Second, the Kekulé structure suggests that benzene should be a highly unsaturated and comparatively unstable compound, in complete contradiction to the observed facts. Since this point has been discussed in considerable detail in various places, we shall not go into it here. The two centric structures (II and III) were proposed to avoid both of the above difficulties. They are indeed successful in eliminating the necessity for the oscillation hypothesis, but they can hardly account for the stability of the molecule. In the Claus structure the diagonal bonds would be very weak, as a result of the large distance between the atoms in the para positions, and the structure would probably represent a molecule less stable even than the Kekulé structure. In the Armstrong-Baeyer structure the meaning of the six lines pointing toward the center is not at all clear. If these

[1] The fourth paper of this series appeared in the J. Am. Chem. Soc. **54**, 3570 (1932).

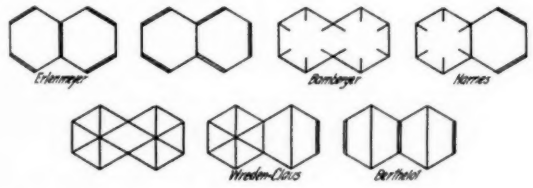
"central bonds" are left undefined, the structure is essentially meaningless; if they are considered to represent free valences, the molecule should be highly unsaturated.

The Dewar structure (IV) has never been seriously considered since it suffers from the same defects, in an accentuated form, as the Kekulé structure. Its advantage over the other structures is largely that it explains the intimate relationship that usually obtains between the para positions in the benzene ring.

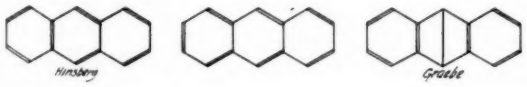
The Ladenburg prism structure (V) can be definitely ruled out, since we know that the benzene ring lies in a plane, or very nearly in a plane. The chemical evidence is also unfavorable in this case.

This by no means exhausts the list of structures proposed for benzene. The remainder, however, such as the structure of Thiele based upon his theory of partial valence and that of Collie based upon a dynamic model, are usually complicated and cannot be represented in any simple valence scheme.

In the case of the aromatic hydrocarbons with condensed ring systems the state of affairs is quite similar. Thus the following structures have been proposed for naphthalene:



for anthracene:



and so on for the other aromatic hydrocarbons. As in the case of benzene, however, the proposed structures are all unsatisfactory, on account both of the non-occurrence of predicted types of isomerism and of the unexpected stability of the molecules.

Apparently here we have a case where the classical ideas of structural organic chemistry are inadequate to account for the observed properties of a considerable group of compounds. With the development of the quantum mechanics and its application to problems of valence and molecular structure, it became evident to workers[2] in this field that the resonance of benzene between the two equivalent Kekulé structures was an essential feature of the structure of this molecule, accounting for the hexagonal symmetry of the ring and for its remarkable stability; and it seemed probable that the quantum mechanical treatment of aromatic molecules would lead to a completely satisfactory explanation of their existence and characteristic properties. E. Hückel[3] has made a valuable start in this direction in a series of papers on the quantum mechanics of benzene. His method of attack, however, is very cumbersome. In this paper we present a treatment of the problem which is rather closely similar to that of Hückel's and which leads to the same result in the case of benzene, but in which the calculations are simplified to such an extent that the method can be extended to the naphthalene molecule without undue labor. Furthermore, with the aid of additional simplifications and approximations we have been able to treat the problem of free radicals and to obtain results in surprisingly good qualitative agreement with experiment. We shall leave the discussion of these latter calculations to the second part of the paper.

We shall set up the problem in essentially the same way as Hückel. We assume that each of the six carbon atoms possesses two K electrons, and four L electrons, one for each of four orbital functions formed by linear combination of the $2s$ and the three $2p$ orbits. Three of these L orbits, each a combination of the $2s$ orbit and the two $2p$ orbits in the plane of the ring, form single bonds to the attached hydrogen atom and the two adjacent carbon atoms. The fourth orbit for each atom remains a pure p-orbit, projecting at right angles to the ring. We neglect the energy of the electrons forming the system of single bonds in the plane and of their interaction with the electrons occupying the pure p-orbits (these energy quantities occurring in the same way for all the structures considered, and hence leading to only a change in the arbitrarily-chosen zero of

[2] As, for example, J. C. Slater, Phys. Rev. **37**, 489 (1931).

[3] E. Hückel, Zeits. f. Physik **70**, 204; **72**, 310 (1931); **76**, 628 (1932).

energy), and consider only the interaction energy of the latter electrons, which may interact with one another in different ways. That is, we treat benzene simply as a six-electron system with spin degeneracy only, and naphthalene as a ten-electron system with spin degeneracy only.

Considerable justification for this choice of orbital functions and of bond distribution is provided by the fact that each of the single exchange integrals between a pure p-orbit and an orbit in the plane of the ring is positive (arising from the e^2/r_{ij} term in the Hamiltonian only), and the chosen distribution of bonds causes these integrals to occur with the negative sign in the expression for the energy of the molecule, while the bonding exchange integrals, which are negative, occur with the positive sign.

In carrying out the calculations we make certain further simplifying assumptions. We neglect all exchange integrals of unity, and all exchange integrals of the energy H except single exchange integrals involving two adjacent atoms. The single exchange integrals involving adjacent atoms, $(abcdef/H/bacdef)$, $(abcdef/H/acbdef)$, etc., are represented by the symbol α. These integrals are seen to be equal in benzene; in naphthalene and other aromatic molecules, in which they are not all required to be equal by the symmetry of the molecule, the reasonable assumption is made that no serious error is introduced by giving them all the same value. The Coulomb integral $(abcdef/H/abcdef)$ is represented by the symbol Q.

Benzene

The benzene molecule can now be treated very simply by the Slater method, with the help of the rules formulated by one of us[4] for finding the matrix elements occurring in the secular equation. The bonds between the six eigenfunctions can be drawn so as to give the independent canonical structures shown in Fig. 1. Any other

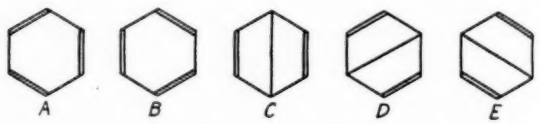
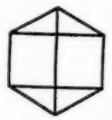


FIG. 1. The five canonical structures contributing to the normal state of the benzene molecule.

structures that can be drawn can be represented by eigenfunctions which are linear combinations of the five above. It will be seen that structures A and B are simply the two Kekulé structures, and C, D and E are three different forms of the Dewar structure. The Claus centric structure does not belong to the canonical set, but it can be represented as a linear combination of canonical structures; and the same is true of the Ladenburg structure if it be considered spread out in a plane, as:



(The Claus structure $=A+B-C-D-E$; the Ladenburg structure $=A+B-D-E$.)

As can be easily verified, the secular equation is

$$\begin{vmatrix} (Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 \\ \frac{1}{4}(Q-W)+3\alpha/2 & (Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 \\ \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & (Q-W) & \frac{1}{4}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 \\ \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & (Q-W) & \frac{1}{4}(Q-W)+3\alpha/2 \\ \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{2}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & \frac{1}{4}(Q-W)+3\alpha/2 & (Q-W) \end{vmatrix} = 0.$$

This quintic equation is easily reduced to three linear factors and one quadratic factor, the roots being -2α, -2α, 0, $(-(13)^{\frac{1}{2}}-1)\alpha$, and $((13)^{\frac{1}{2}}-1)\alpha$. Since α is negative, the last of these roots, $((13)^{\frac{1}{2}}-1)\alpha=2.6055\alpha$, represents the normal state of the molecule. The eigenfunction corresponding to this is (before normalizing) $\psi=\psi_A+\psi_B+0.4341(\psi_C+\psi_D+\psi_E)$. If we had neglected the resonance phenomenon and calculated the energy for one of the structures A or B, we would have obtained the value $W'=Q+1.5\alpha$. Hence the extra energy of the molecule resulting from resonance among the five independent structures

[4] L. Pauling, J. Chem. Phys. 1, 280 (1933).

is 1.1055α. It is interesting to see how much of this extra energy is due to resonance between the two Kekulé structures and how much is contributed by the excited structures *C*, *D* and *E*. A simple calculation shows that 0.9α or approximately 80 percent of the resonance energy comes from the Kekulé structures alone and only about 20 percent from the three excited structures.

In the following paper of this series[5] a value of about 1.7 v.e. has been found from thermochemical data for the resonance energy of benzene. Equating the negative of this quantity to 1.1055α, we calculate the value of α to be about -1.5 v.e. This value may not be very reliable, however, since it is based on the assumption that values of bond energies obtained from aliphatic compounds can be applied directly to aromatic compounds.

The results of the calculation for benzene are summarized in Table I. They are identical with those obtained by Hückel.

The conclusions we draw regarding the structure of the normal benzene molecule are the following. The principal contributions to the structure are made by the two Kekulé structures, resonance between them stabilizing the molecule to the extent of 0.9α or about 1.35 v.e. over a ring with three double bonds. In addition, however, the excited structures contribute appreciably both to the energy (0.2055α) and to the eigenfunction.[6] In a sense it may be said that all structures based on a plane hexagonal arrangement of the atoms—Kekulé, Dewar, Claus, etc.—play a part, with the Kekulé structures most important. It is the resonance among these structures which imparts to the molecule its peculiar aromatic properties.

TABLE I.

	Total energy	Resonance energy	$a : b$
Single Kekulé structure	$Q+1.5\alpha$	0	
Resonance between two Kekulé structures	$Q+2.4\alpha$	0.9α	1 : 0
Resonance among all five structures	$Q+2.6055\alpha$	1.1055α	1 : 0.4341

The ratio $a : b$ is the ratio of the coefficient of structures *A* and *B* to that of the singly-excited structures *C*, *D*, and *E*.

Naphthalene

With naphthalene the calculation is very much more involved. The number of canonical structures is here forty-two (Fig. 2), so that the

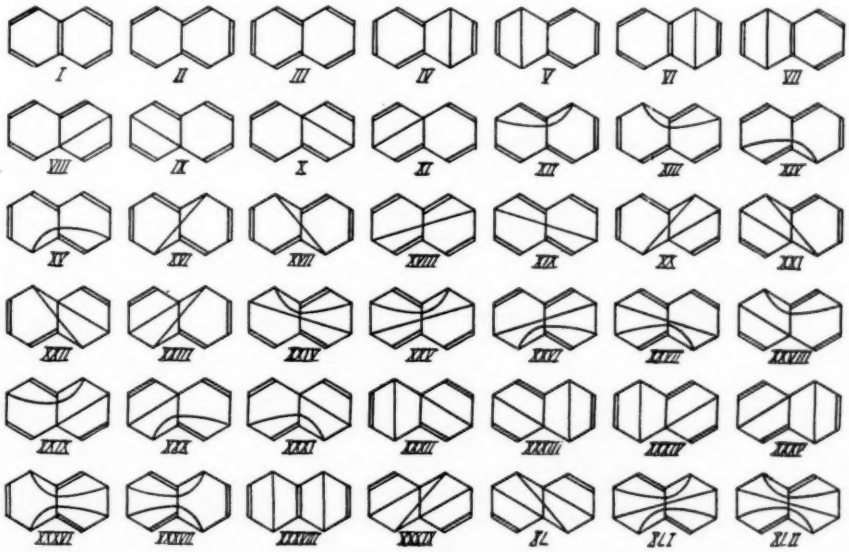


FIG. 2. The forty-two canonical structures contributing to the normal state of the naphthalene molecule.

[5] L. Pauling and J. Sherman, J. Chem. Phys., July, 1933.

[6] The Claus centric structure, an old-quantum-theory analogue of which was suggested several years ago by one of us (L. Pauling, J. Am. Chem. Soc. **48**, 1132 (1926)), is found to make a less important contribution to the normal state of benzene than do the Kekulé structures.

secular equation is of the forty-second degree. We have evaluated the matrix elements in the secular equation by the graphical method, but do not reproduce them because of their great number. For convenience the structures with the maximum number of bonds between adjacent atoms are called unexcited structures and those with one, two, etc., fewer such bonds first excited, second excited, etc., structures. From considerations of symmetry, we can set a number of coefficients equal in the complete eigenfunction, and thereby reduce the secular equation to the fifteenth degree. To obtain an approximate solution of this we then assume that all of the first excited structures have the same coefficient, and similarly for all of the second and all of the third excited structures. The resultant secular equation, corresponding to the function

$$\psi = a\psi_{\mathrm{I}} + b(\psi_{\mathrm{II}} + \psi_{\mathrm{III}}) + c(\psi_{\mathrm{IV}} + \cdots + \psi_{\mathrm{XIX}}) + d(\psi_{\mathrm{XX}} + \cdots + \psi_{\mathrm{XXXVIII}}) + e(\psi_{\mathrm{XXXIX}} + \cdots + \psi_{\mathrm{XLII}})$$

is

$$\begin{vmatrix}
(Q-W)+2\alpha & (1/2)(Q-W)+13\alpha/4 & (35/8)(Q-W)+163\alpha/8 \\
(1/2)(Q-W)+13\alpha/4 & (17/8)(Q-W)+43\alpha/8 & (19/2)(Q-W)+169\alpha/4 \\
(35/8)(Q-W)+163\alpha/8 & (19/2)(Q-W)+169\alpha/4 & (557/8)(Q-W)+2035\alpha/8 \\
(27/8)(Q-W)+165\alpha/8 & (21/2)(Q-W)+159\alpha/4 & (525/8)(Q-W)+2169\alpha/8 \\
(5/8)(Q-W)+31\alpha/8 & 2(Q-W)+7\alpha & (95/8)(Q-W)+397\alpha/8
\end{vmatrix}$$

$$\begin{vmatrix}
(27/8)(Q-W)+165\alpha/8 & (5/8)(Q-W)+31\alpha/8 \\
(21/2)(Q-W)+159\alpha/4 & 2(Q-W)+7\alpha \\
(525/8)(Q-W)+2169\alpha/8 & (95/8)(Q-W)+397\alpha/8 \\
(633/8)(Q-W)+1911\alpha/8 & (57/4)(Q-W)+189\alpha/4 \\
(57/4)(Q-W)+189\alpha/4 & (19/4)(Q-W)-7\alpha/4
\end{vmatrix} = 0.$$

To solve this we first neglect entirely the second and third excited structures. We then solve the secular equation, which is now only a cubic, and evaluate the ratio of the coefficients, $a : b : c$. Finally, we assume that this same ratio holds in the complete eigenfunction, thus obtaining another cubic secular equation, the solution of which is an approximate solution of the original secular equation. The results are summarized in Table II.

TABLE II.

	Total energy	Resonance energy	$a : b : c : d : e$
Single unexcited structure	$Q+2\alpha$	0	1 : 0 : 0 : 0 : 0
Resonance among three unexcited structures	$Q+3.3703\alpha$	1.3703α	1 : 0.8757 : 0 : 0 : 0
Resonance among unexcited and singly excited structures	$Q+3.9760\alpha$	1.9760α	1 : 0.8513 : 0.3026 : 0 : 0
Resonance among all structures	$Q+4.01533\alpha$	2.01533α	1 : 0.8513 : 0.3026 : 0.0919 : 0.0077

It will be noticed that the singly excited structures contribute somewhat over 30 percent to the total resonance energy instead of only about 20 percent as in benzene. The doubly and triply excited structures, however, make only a very small contribution.

Pauling and Sherman have found empirically[5] that the ratio of the resonance energy of naphthalene to that of benzene is 1.90, while the present calculation gives the ratio of 1.82. The agreement is really quite satisfactory. It would have been somewhat, but probably not a great deal, better if the secular equation in the naphthalene calculation had been solved rigorously. The discrepancy must be attributed to the crudity of the method of calculation, and partly

also to the fact that, as mentioned above, the resonance energy calculated by Pauling and Sherman is not strictly comparable with that found by the present method. The value of α obtained from this calculation is -1.6 v.e., in good agreement with the value of -1.5 v.e. obtained from the benzene calculation.

This treatment could be applied to anthracene and phenanthrene, with 429 linearly independent structures, and to still larger condensed systems, though not without considerable labor. It is probable that the empirical rule[5] of approximate proportionality between the resonance energy and the number of benzene rings in the molecule would be substantiated.

The Structure and Stability of Hydrocarbon Free Radicals

The dissociation of a hexaarylethane into free radicals,

$$R_3C-CR_3 \rightarrow 2R_3C-,$$

first observed by Gomberg about thirty years ago, can be considered formally to take place in two steps. First, the bond connecting the two halves of the original molecule breaks; and second, the free radicals formed thereupon stabilize themselves to a certain extent by means of a change in structure. Most theories which have been proposed to explain the existence and stability of free radicals have more or less tacitly assumed that the first of these steps is of primary importance and that the influence of the second upon the dissociation is negligible in comparison. Consequently these theories have concerned themselves very largely with attempts to explain why the ethane linkage in the undissociated molecule should be weakened by the presence of aryl groups. Of these various attempts, two stand out most prominently, one based upon the theory of "affinity-demand" (Valenzbeanspruchung), and the other upon the consideration of steric influences. According to the theory of affinity-demand, the aryl groups use up so much of the available affinity of the methyl carbon atoms that there is very little left over for the ethane linkage. This is not a very satisfactory explanation, however, for several reasons. It does not show why aryl groups should have such a great affinity-demand—as compared, for example, with alkyl groups, nitro groups, etc.—nor does it enable one to predict which aryl groups should be relatively more effective and which relatively less effective in promoting dissociation. Furthermore, it leads to definitely incorrect predictions in some cases. Thus, tetraphenylmethane would be expected to be rather unstable, while actually it is an extraordinarily stable compound, boiling at 431° without decomposition.

The steric theory of free radical dissociation is based upon the assumption that the aryl groups are so large that they prevent the two halves of the undissociated molecule from coming close enough together to permit the formation of a strong bond. There are, however, some difficulties with this explanation as well. It is roughly true, to be sure, that the effectiveness of a group in promoting free radical dissociation runs parallel to its size, but why, for example, should the linear biphenyl group have a greater steric effect than the phenyl group, and why should there be an appreciable difference between the α and the β-naphthyl groups? In addition the stability of tetraphenylmethane is about as irreconcilable with this theory as with that of affinity-demand.

We may conclude from this discussion that it is apparently impossible to base a satisfactory theory of the free radicals upon the assumption that the C—C bond in the undissociated molecule is weakened by the influence of the aryl groups. We avoid the necessity of making this assumption, however, by considering that the energy necessary to carry through the first step of breaking the bond is the same in all cases, but that the subsequent stabilization of the radicals, resulting from the second step of changing the structure, may vary widely. Thus we attribute the dissociation not to the instability of the undissociated molecule but to the stability of the radicals formed in the dissociation.

This idea has been developed by Burton and Ingold,[7] but not upon a very satisfactory theoretical basis. From their work it is not clear why the postulated redistribution of charge should occur after, but not before, dissociation,

[7] H. Burton and C. K. Ingold, Proc. Leeds Phil. Soc. **1**, 421 (1929); C. K. Ingold, Ann. Reports Chem. Soc. **25**, 154 (1928).

nor is the mechanism by which this redistribution stabilizes the radical definitely established. In the following pages we describe the extension to the free radical problem of the quantum-mechanical methods which we used with benzene and naphthalene. It is shown that a straightforward calculation of the resonance energy for the undissociated ethane and for the free radical leads to values of the dissociation energy of various substituted ethanes in excellent qualitative and semiquantitative agreement with experiment. This theory of the stability of free radicals may be considered as a refinement and extension of Burton and Ingold's general views, for which it provides a sound theoretical basis.

Before going into our methods of calculation we shall first discuss briefly the nature of the experimental results which we wish to explain. In spite of the vast amount of work which has been done on free radicals in the last thirty years, the information available regarding the degree of dissociation of most hexaarylethanes is meager, and exceedingly inaccurate. Ziegler and Ewald[8] have carried out precise photometric determinations in the cases of hexaphenylethane and tetraphenyldi-β-naphthylethane. In other cases the only data at hand are derived from determinations of the apparent molecular weights by the cryoscopic method. That this method is undependable is shown by the fact that it frequently indicates degrees of dissociation of 130 percent or even higher, and in the case of the slightly dissociated tetraphenyldi-β-naphthylethane it indicates a degree of dissociation two or three times greater than that found by Ziegler and Ewald. In some cases even this source of information is lacking, and then recourse must be had to such data as the intensity of the color of solutions, the temperature at which the color first appears, the number of times the color will reappear after having been discharged with air, the rate of absorption of oxygen, and so on. Obviously such methods can give only the crudest of results. As a further complication we have the fact that the degree of dissociation of a given ethane varies considerably with temperature, with solvent, and with concentration, and frequently the determinations have not been made under comparable conditions. In spite of all these difficulties, however, we can say with some assurance that the tendency toward dissociation increases in the following order: any ethane with less than six aryl groups $\ll$ diphenyldifluoryl $\ll$ hexaphenylethane $<$ tetraphenyldi-β-naphthylethane $<$ tetraphenyldi-α-naphthylethane $\leqq$ diphenyltetrabiphenylethane $<$ hexabiphenylethane. We have intentionally omitted tetraphenyldibiphenylethane from this list since we do not consider that its degree of dissociation has been measured with sufficient accuracy to warrant its inclusion. It has been studied neither photometrically nor cryoscopically, and so the estimate of 15 percent dissociation usually given in the literature is not to be taken very seriously. In most lists like the above it occupies a position between hexaphenylethane and tetraphenyldi-β-naphthylethane.

From such crude data as are to be found in the literature we can calculate approximate values of the equilibrium constants, and hence of the free energies of dissociation for the various hexaarylethanes. From our quantum-mechanical treatment, on the other hand, we obtain only the heats of dissociation, for which, except in the single case of hexaphenylethane, we have no experimental data. Thus, in order that we may compare our results with those of experiment, we must make the plausible assumption that the entropies of dissociation vary only slightly from ethane to ethane. Then at a given temperature the heats of dissociation run parallel to the free energies and can be used instead of the latter in predicting the relative degrees of dissociation of the different molecules.

In carrying out the calculations we use essentially the same procedure as in the case of benzene and naphthalene. As an additional simplification, however, we neglect entirely all the excited states of the molecule, since their contribution to the total energy is comparatively small, and since they would complicate the calculations tremendously if retained. Another slight modification of the procedure is necessitated by the fact that a free radical possesses an odd number of electrons, one of which must remain unpaired. This is taken care of formally by introducing a "phantom orbit" X with an accompanying "phantom electron" which is paired with the odd electron.[4] In the subsequent

[8] K. Ziegler and L. Ewald, Ann. **473**, 179 (1932).

calculations it is necessary merely to remember that all exchange integrals which involve the phantom orbit vanish. The rules for setting up the matrix elements and the secular equations are otherwise unchanged.

We shall discuss in detail only one example, and for the sake of simplicity we shall take the (actually undissociated) sym. diphenylethane. Let us first consider what happens when the ethane dissociates. In the first step, the C−C bond breaks and there are formed two phenylmethyl radicals, which however can resonate between only the structures A and B of Fig. 3.

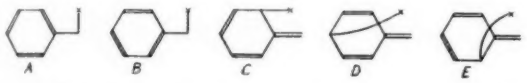


FIG. 3. The five unexcited canonical structures contributing to the normal state of the phenylmethyl radical.

ΔH for this reaction we take to be 3.65 v.e., the energy required to break a C−C bond in aliphatic compounds. The second step of the dissociation consists in a change in the structure of the radicals, involving a change in nuclear configuration from a tetrahedral arrangement of bonds about the methyl carbon to a plane arrangement of all the nuclei, and in electronic structure through the removal of the restriction of the resonance to the structures A and B, all five of the canonical structures being now allowed. ΔH for this reaction is just twice the difference between the energies of a single radical after and before the removal of the restriction. The energy change for the over-all reaction is then the algebraic sum of the energy changes of the two steps.

To evaluate ΔH for the second step we must set up and solve the secular equations corresponding to the two different states of the radical. In the case where we consider only the structures A and B the secular equation is easily shown to be:

$$\begin{vmatrix} (Q-W')+\alpha & \frac{1}{4}(Q-W')+11\alpha/8 \\ \frac{1}{4}(Q-W')+11\alpha/8 & (Q-W')+\alpha \end{vmatrix}=0.$$

On solving this we find for the energy $W'=Q+1.9\alpha$, and for the wave function $\psi'=a(\psi_A+\psi_B)$ where a is a normalization factor.

When we consider resonance between all five structures we obtain a quintic secular equation:

$$\begin{vmatrix} (Q-W)+\alpha & \frac{1}{4}(Q-W)+11\alpha/8 & \frac{1}{8}(Q-W)+7\alpha/8 & \frac{1}{4}(Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 \\ \frac{1}{4}(Q-W)+11\alpha/8 & (Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & \frac{1}{4}(Q-W)+\alpha & \frac{1}{8}(Q-W)+7\alpha/8 \\ \frac{1}{8}(Q-W)+7\alpha/8 & \frac{1}{2}(Q-W)+5\alpha/2 & (Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & \frac{1}{4}(Q-W)+\alpha \\ \frac{1}{4}(Q-W)+\alpha & \frac{1}{4}(Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & (Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 \\ \frac{1}{2}(Q-W)+5\alpha/4 & \frac{1}{8}(Q-W)+7\alpha/8 & \frac{1}{4}(Q-W)+\alpha & \frac{1}{2}(Q-W)+5\alpha/4 & (Q-W)+\alpha \end{vmatrix}=0.$$

This can be simplified to a cubic equation since from considerations of symmetry it follows that the coefficients of ψ_A and of ψ_B must be the same in the complete function, and similarly for ψ_C and ψ_E. We shall however, make a further simplification by assuming that ψ_D has the same coefficient as ψ_C and ψ_E, and thereby reduce the secular equation to a quadratic:

$$\begin{vmatrix} (5/2)(Q-W)+19\alpha/4 & (7/4)(Q-W)+25\alpha/4 \\ (7/4)(Q-W)+25\alpha/4 & (11/2)(Q-W)+10\alpha \end{vmatrix}=0.$$

On solving this we find for the energy $W=Q+2.4092\alpha$, and for the wave function $\psi=a(\psi_A+\psi_B)+b(\psi_C+\psi_D+\psi_E)$ where a and b are in the ratio $a:b=1:1.0279$. The "free radical resonance energy" is thus $W-W'=0.5092\alpha$, and ΔH for the dissociation is equal to 3.65 v.e.$+2\times0.5092\alpha=3.65$ v.e.$+1.0184\alpha$. As we shall show later, the value of α is probably about -1.4 v.e., and so the heat of dissociation of sym. diphenylethane is approximately 2.2 v.e., a value in good

accord with the vanishingly small degree of dissociation. In view of the uncertainty connected with the values of α and of the C–C bond energy we shall as a rule not calculate the heats of dissociation of the remaining ethanes, but instead shall use as a criterion of the tendency of a given compound to dissociate simply the coefficient of α in the expression for the free radical resonance energy. It will be noted that on account of the negative sign of α the dissociation increases as this coefficient increases.

The results obtained from this and from similar calculations for a number of other free radicals are summarized in Table III. In the first

TABLE III.

Radical	W'	W	$W-W$
Phenylmethyl	$Q+1.9000\alpha$	$Q+2.4092\alpha$	0.5092α
Biphenylmethyl	$Q+3.8000\alpha$	$Q+4.3568\alpha$	0.5568α
β-Naphthylmethyl	$Q+2.8703\alpha$	$Q+3.5012\alpha$	0.6309α
α-Naphthylmethyl	$Q+2.8703\alpha$	$Q+3.6218\alpha$	0.7515α
Fluoryl	$Q+3.3000\alpha$	$Q+4.1004\alpha$	0.8004α
Diphenylmethyl	$Q+3.8000\alpha$	$Q+4.6409\alpha$	0.8409α
Phenylfluoryl	$Q+5.2000\alpha$	$Q+6.2764\alpha$	1.0164α
Triphenylmethyl	$Q+5.7000\alpha$	$Q+6.8078\alpha$	1.1078α
Biphenyldiphenylmethyl	$Q+7.6000\alpha$	$Q+8.7310\alpha$	1.1310α
Phenyldibiphenylmethyl	$Q+9.5000\alpha$	$Q+10.6545\alpha$	1.1545α
Tribiphenylmethyl	$Q+11.4000\alpha$	$Q+12.5773\alpha$	1.1773α
β-Naphthyldiphenylmethyl	$Q+6.6636\alpha$	$Q+7.8351\alpha$	1.1715α
α-Naphthyldiphenylmethyl	$Q+6.6636\alpha$	$Q+7.9033\alpha$	1.2398α

column we have listed the radical under consideration; in the second, the energy W' calculated for the radical with resonance restricted to the structures in which the unpaired electron is on the methyl carbon atom; in the third, the energy W calculated for the radical with resonance allowed among all possible states; and in the fourth, the free radical resonance energy $W-W'$.

Mention may be made of a special method developed for setting up the secular equation for free radicals. The direct calculation of matrix elements, even by the simple graphical method, would be extremely laborious for such a radical as tribiphenylmethyl, for example, for which 496 structures are taken into consideration. Let us consider three superposition patterns, each consisting of one of the substituent groups in the free radical plus the methyl carbon and the phantom orbit, the corresponding Coulomb and exchange coefficients being q_1, q_2, q_3 and a_1, a_2, a_3, respectively. It is easily proved that the Coulomb coefficient q and the exchange coefficient a for the entire superposition pattern have the values

$$q=q_1q_2q_3$$

and

$$a=a_1q_2q_3+q_1a_2q_3+q_1q_2a_3.$$

For a set of superposition patterns obtained by combining a set for each of the three groups in all possible ways, the sums of the coefficients (for equal weights of the corresponding structures) are

$$\Sigma q=\Sigma q_1\cdot\Sigma q_2\cdot\Sigma q_3$$

and

$$\Sigma a=\Sigma a_1\cdot\Sigma q_2\cdot\Sigma q_3+\Sigma q_1\cdot\Sigma a_2\cdot\Sigma q_3+\Sigma q_1\cdot\Sigma q_2\cdot\Sigma a_3.$$

As an example we may use these equations to calculate the coefficients summed over the 64 matrix elements corresponding to the eight structures of triphenylmethyl with the unpaired electron on the methyl carbon. Reference to the secular equation for phenylmethyl shows that $\Sigma q_1=\Sigma q_2=\Sigma q_3=1+1+\frac{1}{4}+\frac{1}{4}=5/2$, and $\Sigma a_1=\Sigma a_2=\Sigma a_3=11/4$, leading to the values $\Sigma q=125/8$ and $\Sigma a=1425/16$.

The secular equations which must be solved for the values of W are frequently of very high degree, even after all of the simplifications arising from considerations of symmetry have been introduced. In such cases we have reduced the equations to cubics (sometimes to quadratics) by equating coefficients in a more or less arbitrary

manner. The calculated values for the free radical resonance energy are, therefore, uncertain to the extent to which they are affected by this not strictly legitimate simplification. We feel, however, that the errors introduced in this way are not very large, since we have found by actual calculation in two cases that the energies are not very sensitive to small changes in the coefficients. For example, the energy W of the triphenylmethyl radical is given in Table III as $Q+6.8078\alpha$. This was obtained by solving rigorously the secular equation, which in this case could be reduced to a cubic. If, on the other hand, we equate all coefficients and make the equation linear, we obtain for W the value $Q+6.8064\alpha$. In the case of the α-naphthyldiphenylmethyl radical the value of $Q+7.9033\alpha$ given for W in Table IV was derived from a cubic

TABLE IV.

Radical	Position of odd electron	Number of structures	Relative values of coefficients
Phenylmethyl	methyl carbon	2	1
	phenyl group	3	1.0279
Biphenylmethyl	methyl carbon	4	1
	biphenyl group	9	0.4526
β-Naphthylmethyl	methyl carbon[a]	1	1
	methyl carbon[b]	2	0.8789
	naphthyl group	6	0.5458
α-Naphthylmethyl	methyl carbon[a]	1	1
	methyl carbon[b]	2	0.8828
	naphthyl group	7	0.5916
Fluoryl	methyl carbon	4	1
	biphenylene group[c]	8	0.6768
	biphenylene group[c]	4	0.6056
Diphenylmethyl	methyl carbon	4	1
	phenyl group	12	0.7232
Phenylfluoryl	methyl carbon	8	1
	phenyl group	12	0.8983
	biphenylene group	24	0.8430
Triphenylmethyl	methyl carbon	8	1
	phenyl group (para)	12	0.8829
	phenyl group (ortho)	24	0.9896
Biphenyldiphenylmethyl	methyl carbon	16	1
	phenyl group	48	0.8546
	biphenyl group	36	0.6477
Phenyldibiphenylmethyl	methyl carbon	32	1
	phenyl group	48	0.7881
	biphenyl group	144	0.5969
Tribiphenylmethyl	methyl carbon	64	1
	biphenyl group	432	0.5535
β-Naphthyldiphenylmethyl	methyl carbon	12	1
	phenyl group	36	0.9085
	naphthyl group	24	0.8497
α-Naphthyldiphenylmethyl	methyl carbon	12	1
	phenyl group	36	0.9200
	naphthyl group	28	0.9121

[a] With the naphthyl group symmetrical as in structure I, Fig. 2.
[b] With the naphthyl group unsymmetrical as in structures II and III, Fig. 2.
[c] The distinction between these two types of structure is described below in the discussion of the fluoryl radical.

equation, obtained by equating the coefficients of all structures in which the odd electron is (1) on the methyl carbon atom, (2) on the naphthyl group, and (3) on a phenyl group. If the equation is reduced further to a quadratic by equating the coefficients of all structures of the last two types the energy W is changed only in the fifth decimal. The effect of these errors which, though small, are sometimes quite appreciable will always be to make the value of W too large (that is, the coefficient of α too small). Since the secular equations for W' can be solved rigorously in all cases, this will cause the radicals to appear less stable relative to the ethanes than they should. This effect should be particularly pronounced in the cases of the α- and the β-naphthyldiphenylmethyl radicals because of the high degree of the secular equations. Furthermore, in these radicals we have had to give the structures in which the naphthyl group has the symmetrical form (as in structure I, Fig. 2) the same coefficient as the structures in which the naphthyl group has the unsymmetrical form (as in structures II and III, Fig. 2), and this simplification seems to be particularly unjustified. At any rate it is found to be pretty far off in the cases of the simple α and β-naphthylmethyl radicals where the calculations have been carried through somewhat more rigorously. This error has been partially corrected by making the same approximation in the calculations of W'; that is, by putting all coefficients equal and solving linear instead of quadratic secular equations.

In order to make clear the manner in which we have simplified the treatment of the various radicals, we give in Table IV a statement of the value and significance of the coefficients occurring in the function ψ in the individual cases. It will not be necessary to give a similar table for the functions ψ' since, except in the cases of the α and the β-naphthyldiphenylmethyl radicals which have been discussed above, no simplifications were necessary for them, and the secular equations were solved rigorously.

Discussion of results

The principal source of inaccuracy in the treatment given the free radicals is the neglect of all excited structures. In the case of benzene the three excited structures contribute 0.2055α to the resonance energy, which is about 20 percent of the total resonance energy of the molecule. The same error is introduced in W' for the phenylmethyl radical. The change in W produced by the inclusion of the nine excited structures as well as the five unexcited structures is not so large, so that $W-W'$ is decreased from 0.5092α to 0.4455α, a decrease of 0.06α or 12 percent of $W-W'$. Similar changes in the values of $W-W'$ would result from the consideration of excited structures for other radicals. In consequence, so long as excited structures are not included in the treatment the values of $W-W'$ cannot be considered to be accurate to 10 percent. This does not prevent us from making use of the values given in Table III, however, in certain cases. Thus for each of the radicals included in the table the value of $W-W'$ can be considered to give the extra resonance energy stabilizing the radical with an accuracy of 10–20 percent. Moreover, in some cases differences in the $W-W'$ values for different radicals can be trusted to the same extent; namely, when one radical differs from another only by the addition of a group, so that all of the structures considered for the first radical are retained for the second, as well as other structures. Thus the difference of the $W-W'$ values for biphenylmethyl and phenylmethyl should give with considerable accuracy the extra stability resulting from the substitution of biphenyl for phenyl, and a similar comparison should be reliable for α-naphthyl and β-naphthyl, α or β-naphthyl and phenyl, fluoryl and diphenyl, etc., but not for α-naphthyl and biphenyl, inasmuch as in these completely different groups the effect of neglect of excited structures may well mask the small differences under consideration. When this restriction in the interpretation of the $W-W'$ values is borne in mind, it is found that the agreement between the rather rough theoretical calculations and the existent empirical information is excellent, and provides sound evidence that resonance of the type considered is the primary factor in the stabilization of the hydrocarbon free radicals. A number of details in the comparison are treated in the following paragraphs.

(a) The calculation for triphenylmethyl leads to a value of 3.65 v.e.$+2.2156\alpha$ for the heat of dissociation of hexaphenylethane. Equating this to the experimentally determined value of 0.5

v.e., we obtain as a result that $\alpha = -1.4$ v.e. This is in fair agreement with the value of -1.5 v.e. obtained from the calculation for benzene; the discrepancy may be due in part to the fact mentioned before that the evaluation of α from the benzene calculation is not strictly legitimate, and in part to the neglect of excited structures, which (from analogy with phenylmethyl) are expected to decrease the coefficient of α in $W-W'$, and so increase the absolute value of α.

(b) Except for comparisons of naphthyl and biphenyl, the amounts of dissociation indicated by the values of $W-W'$ for various radicals are in excellent qualitative agreement with experiment. It is undoubtedly significant that, as is demanded by experiment, the variations in the free radical resonance energies obtained by increasing the number of aryl groups is large compared with the variations obtained by changing the nature of the groups already present.

(c) In order to make a quantitative comparison of our results with experiment, let us calculate the ratio of the dissociation constants corresponding to a difference in the free radical resonance energies of 0.01α. If we let the subscript 1 refer to the more highly dissociated ethane and 2 to the less highly dissociated, we have the following relation:

$$RT \ln (K_2/K_1) = \Delta F_1 - \Delta F_2 \cong \Delta H_1 - \Delta H_2 = 0.02\alpha.$$

Since α is equal to -1.4 v.e. or $-32{,}000$ calories per mole, this equation becomes

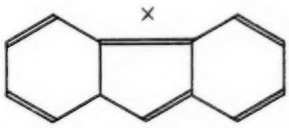
$$RT \ln (K_1/K_2) = 640 \text{ cal./mole}$$

which at 20°C leads to

$$\ln (K_1/K_2) = 1.1 \quad \text{or} \quad K_1/K_2 = 3.0.$$

From Table III we see that the difference between the free radical resonance energies of tribiphenylmethyl and triphenylmethyl is 0.07α. Hence $K_1/K_2 = 3^7 = 2.2\times10^3$. Ziegler and Ewald[8] found that at 20°C the value of the dissociation constant for hexaphenylethane in benzene solution is 4.1×10^{-4} and consequently we calculate for hexabiphenylethane a value of $K = 2.2\times10^3 \times 4.1\times10^{-4} = 0.90$. This value is probably too low as the compound is reported to be completely dissociated; the error may not be large, however, since a dissociation constant of 0.90 would lead to 91 percent dissociation in $0.05M$ solution. The solutions actually worked with have usually been more dilute than this, and so our calculated value may be within the experimental error.

(d) The ability of the present method to distinguish between apparently small differences in structure is brought out forcibly by a comparison of the relative effectiveness of the α- and the β-naphthyl groups on the one hand, and of the fluoryl and the diphenylmethyl groups on the other. The greater dissociating power of α-naphthyl is qualitatively correlated with the fact that for it there are seven unexcited structures with the odd electron on a naphthyl carbon, whereas there are only six for β-naphthyl. The case of fluoryl is particularly striking. For the fluoryl radical it is possible to write six more unexcited structures than for the diphenylmethyl radical. These extra structures are all of the type



That is, they all have a double bond in the ortho linkage between the phenyl groups, and they all have the odd electron on one or the other of the phenyl groups. Hence it would seem that the radical should be stabilized by these extra possibilities of resonance, while the ethane should be left practically unaltered, and that consequently the dissociation should be increased. Actually, however, the opposite is the case. On putting in the phantom orbit and drawing all the bonds it is found that no matter where the phantom orbit is put with respect to the other orbits all the possible structures cannot be made canonical simultaneously. There will always be six non-canonical structures which must be represented as linear combinations of the canonical ones, and so the structures suggesting extra resonance are eliminated. Just which six structures are non-canonical will depend upon the position given the phantom orbit. If it be put in the symmetrical position indicated above, the non-canonical structures will be those in which there is a double bond between the two phenyl groups. Two of these structures turn out to be combinations of excited structures and so are neglected. The remaining four are combinations of one unexcited and one excited structure each.

These excited structures are also neglected, and the four unexcited structures are distinguished from the remaining eight by being given a different coefficient. This is the reason for the fact noted in Table IV that for the fluoryl radical there are three instead of two coefficients. Since, however, the coefficients for the two different types of structures proved to be nearly the same here, they were put equal to each other in the calculation for the phenylfluoryl radical. This explains why the fluoryl group should not be more effective in promoting dissociation than the diphenylmethyl group, but to see why it is actually less effective we must turn our attention to the rules by which the matrix elements are calculated. Since we have shown that we can eliminate all the extra resonance structures of the fluoryl radical, the structures which we have left are exactly the same as those in the case of diphenylmethyl, except for the ortho bond between the two phenyl groups. Therefore the secular equation is the same except for the effect of the interchange integral between the atoms at either end of the bond, and this integral will always come into the matrix elements with a negative sign. Consequently the coefficient of α in any given matrix element for the fluoryl radical will be less than in the corresponding element for the diphenylmethyl radical. As a result of this, the coefficient of α will be decreased in both the energies W and W', and since this decrease is greater in the former case than in the latter, the coefficient in the extra resonance energy $W-W'$ will also be decreased.

(e) Although the theory described in this paper is able to explain qualitatively and semi-quantitatively the dissociation of a considerable number of free radicals, it proves to be definitely inadequate in some cases. For example, di-tert.-butyl-tetraphenylethane has been found to be appreciably dissociated at room temperature, although our calculation would give exactly the same value of the free radical resonance energy as in the case of the undissociated tetraphenyl-ethane, since the presence of the tert. butyl group does not affect the number of resonating structures nor the values of the matrix elements. The same considerations also apply to decaphenyl-butane, which has been found to be completely dissociated into pentaphenylethyl radicals. We consider that in these cases the steric effect may enter and be of dominating importance. There is no doubt that the tert. butyl and the triphenyl-methyl groups are relatively large, and their presence in these compounds may tend to keep the radicals apart.

Furthermore, there are a number of interesting free radicals other than the hydrocarbons to which our treatment could be extended. In order to carry through similar calculations for compounds containing oxygen or nitrogen, however, we would have to introduce a number of additional parameters, corresponding to exchange integrals other than that to which we have given the value of α, which would make the calculations more difficult and the results less valuable.

Mention may be made of the interesting observation of Wieland that triphenylmethyldi-*p*-anisylamine does not dissociate appreciably except at temperatures above 140°

$$(C_6H_5)_3C-N(C_6H_4OCH_3)_2 \rightleftarrows (C_6H_5)_3C-+-N(C_6H_4OCH_3)_2$$

although the free radicals formed can exist to an appreciable extent in the monomeric form even at room temperature—a fact which has excited considerable comment. The explanation does not involve a difference in resonance in this compound and the corresponding ethane and hydrazine, but instead a difference in the energy of the carbon-nitrogen bond and the mean for the carbon-carbon and nitrogen-nitrogen bonds, resulting from additional ionic character of the unsymmetrical bond. This amounts to about 0.5 v.e.,[9] and so is large enough to prevent dissociation.

On the other hand, the stability of positive and negative triarylmethyl ions is due to the same resonance effect as that of the neutral radicals discussed in this paper.

[9] See the preceding and the following paper of this series.

Predissociation and the Crossing of Molecular Potential Energy Curves

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The calculation of the width and shape of a line which is broadened because of predissociation has been extended so as to include perturbations of intermediate size. By "perturbations of intermediate size" we mean perturbations which are not so great that lines (of given rotational quantum number) belonging to two adjacent vibrational levels are broadened so as to overlap appreciably; they may be any size up to that limit. These calculations have been applied with certain simplifying assumptions to the case where a potential curve giving molecule formation is intersected by a repulsive curve, the curves which cross defining the unperturbed energy levels and wave functions. It is found that the discrete lines are not only broadened, but they are shifted in position, slightly distorted in shape, and there is present a series of subsidiary maxima of the absorption coefficient. The exact amount of broadening of a line depends very greatly upon its energy relative to the energy at which the potential curves cross, and in general a line which is much broadened will also be much shifted in position. In molecules we may expect to have isolated groups of rotational levels in which the central level is sharp, and the rotational levels on either side become more and more diffuse, finally fading out. The predissociation phenomena in iodine chloride are discussed on the basis of the above theory. In particular, two groups of sharp and diffuse levels, such as described, are considered and are respectively ascribed to the isotopic molecules, ICl^{35} and ICl^{37}. There is some difficulty in describing the phenomena in iodine chloride quantitatively, but qualitatively the experimental results appear to accord with the theory.

THE question of what happens when two potential energy curves of a diatomic molecule cross has interested spectroscopists for some time. The Franck-Condon principle, so useful in explaining intensities in band spectra, says, when applied to the case of radiationless transitions such as occur for example in predissociation, that transitions are likely to occur from the electronic state corresponding to one potential energy curve to the electronic state corresponding to the other if the total energy of the system is about equal to the energy at which the two curves cross. This principle has been used by Herzberg[1] and others to explain the variation in the widths of the rotation lines in various cases of predissociation. Nevertheless, little quantitative work has been done on the subject. It is the purpose of this article to investigate quantitatively just what does happen in the neighborhood of the crossing point of two potential energy curves in a particularly simple case of predissociation. We shall find that a given rotation level is not only broadened, but is somewhat distorted in shape, is shifted in position, and has a rather complicated secondary structure. An attempt will then be made to apply the results to the case of predissociation in iodine chloride, observed by Brown and Gibson.[2]

§1. General Theory

The phenomenon of predissociation, first discovered by Henri and Teves,[3] was explained as a sort of molecular Auger process by Bonhoeffer and Farkas,[4] and considered from a quantum mechanical point of view by Kronig.[5] I discussed it further,[6] and gave a fairly rigorous derivation of the formula for the amount of broadening of the rotation lines as a function of the perturbation matrix component of the disturbance causing the effect. In order to handle the present situ-

[1] See Herzberg, Zeits. f. Physik **61**, 604 (1930); Ergeb. d. exacten Naturwiss. **10**, 237 (1931). Other references are given in the latter article. The question has been treated from another point of view by London, Zeits. f. Physik **74**, 158 (1932). In this connection see also, Neumann and Wigner, Phys. Zeits. **30**, 467 (1929), and Zener, Proc. Roy. Soc. (London) **A137**, 696 (1932).

[2] Brown and Gibson, Phys. Rev. **40**, 529 (1932).

[3] Henri and Teves, Nature **114**, 894 (1924).

[4] Bonhoeffer and Farkas, Zeits. f. physik. Chemie **134**, 337 (1928).

[5] Kronig, Zeits. f. Physik **50**, 360 (1928). See also Wentzel, Zeits. f. Physik **43**, 524 (1927); Fues, Zeits. f. Physik **43**, 726 (1927); Wentzel, Réunion Internationale de Chimie Physique, Paris, 1928, p. 121.

[6] Rice, Phys. Rev. **33**, 748 (1929); **35**, 1551 (1930).

ation, some of the approximations and specializations made in this theory need to be removed, and to this task we now address ourselves.

We consider a diatomic molecule, or a pair of atoms, and make use of an approximate wave function, ψ, which may be written in the form

$$\psi = \Theta R. \tag{1}$$

Here Θ is the wave function for the electrons and the rotation, obtained by holding the distance, r, between the two nuclei fixed. It depends therefore on the rotational and electronic coordinates, and on r only as a parameter. R is the radial part of the wave function and is a function only of r, though it depends on the quantum numbers of Θ.

A Θ belonging to a given electronic and rotational state of the molecule, distinguished by a subscript, say k, will obey an equation of the form

$$(H_0 - U_k)\Theta_k = 0, \tag{2}$$

where H_0 is the Hamiltonian operator for the electronic and rotational coordinates, and U_k (a function of r) is the energy.

A given R which goes with Θ_k, say R_{km}, may be written in the form F_{km}/r, where F_{km} obeys the equation

$$d^2F_{km}/dr^2 + \eta^2(E_{km} - U_k)F_{km} = 0, \tag{3}$$

where $\eta^2 = 8\pi^2M/h^2$, and M is the reduced mass of the system.

We now write, in formal fashion, the wave equation which is obeyed by the approximate wave function $\psi_{km} = \Theta_k F_{km}/r$ as

$$(H - E_{km})\psi_{km} = 0. \tag{4}$$

But this cannot be an exact equation. At the very best, in separating the electronic and rotational coordinates from the coordinate r we have made an approximation. We shall let an exact wave function ψ' obey the equation

$$(H + V - E')\psi' = 0, \tag{5}$$

where V is a perturbation term and E' the perturbed energy.

We now come more specifically to the consideration of a particular case in which predissociation may occur. We will suppose that we have two potential energy curves U_1 and U_2 with corresponding wave functions Θ_1 and Θ_2. We further suppose that U_1 is the repulsive type curve, or else that we are interested in an energy region above its energy of dissociation, while U_2 is the type giving molecule formation and we are below its dissociation energy. Any R, let us say R_{2d}, or simply R_d, which goes with U_2 will be an eigenfunction belonging to a discrete state, while those which go with U_1, designated in general by R_s will form a continuous set. To normalize these we shall assume that r has a largest possible value which we shall call r_∞; this converts the continuous set of energy levels to a very close-spaced discrete set, the energy, ϵ_s, between two adjacent "continuous" levels being given by

$$\epsilon_s = 2\pi(E_s - U_1(\infty))^{\frac{1}{2}}/r_\infty\eta, \tag{6}$$

where E_s is the energy of the continuous state and $U_1(\infty)$ is the asymptotic value of U_1. We normalize R_s by setting

$$\int_0^{r_\infty} R_s^2 r^2 dr = \int_0^{r_\infty} F_s^2 dr = 1. \tag{7}$$

Now the interaction, represented by the perturbation V, causes, as is well known, an effective "broadening" of the discrete states. That is, in the exact wave function, ψ', which can be set up as a linear function of discrete and continuous states, the coefficient of a given discrete state has an appreciable value over a certain finite energy range in the neighborhood of the original energy, E_d. By solving the perturbation problem one is able to find the "width" of these broadened discrete states. We define certain matrix components, as follows,

$$v_{11} = \int \Theta_1^* V \Theta_1 d\tau, \quad v_{22} = \int \Theta_2^* V \Theta_2 d\tau, \tag{8}$$

$$v_{12} = \int \Theta_1^* V \Theta_2 d\tau = \int \Theta_2^* V \Theta_1 d\tau, \tag{9}$$*

$$v_{ss} = \int_0^{r_\infty} F_s v_{11} F_s dr, \quad v_{dd} = \int_0^{r_\infty} F_d v_{22} F_d dr, \tag{10}$$

$$v_{sd} = \int_0^{r_\infty} F_s v_{12} F_d dr, \tag{11}$$

* We assume v_{12} real. If it is not the necessary modification may be readily made.

the integrals (8) and (9) being taken over all possible volume elements, $d\tau$, in the coordinate space defining the Θ's, and the asterisk denoting the conjugate complex. If we assume v_{11} and v_{22} absorbed into U_1 and U_2, respectively, (we shall write V_1 to mean U_1+v_{11} and similarly with V_2) then it may be readily shown[7] that the matrix components v_{ss} and v_{dd} do not enter into the problem and the only ones we have to consider are those of the type v_{sd}.

We consider the case where the discrete states are so far apart in comparison to the broadening suffered by them that we need to take into account only one of them at a time.[8] This is, of course, a restriction on the size of the perturbations, but the only one necessary to make; such perturbations may be called "perturbations of intermediate size." We also make the assumption that there is only one set of continuous states involved. We can then write for a particular ψ', say ψ_n,

$$\psi_n = S_{dn}\psi_d + \sum_s S_{sn}\psi_s \tag{12}$$

ψ_d and ψ_s being written for the complete wave functions of form (1) corresponding respectively to the discrete state and to the continuous states. If E_n is the energy that goes with ψ_n, then one may show, by application of the perturbation theory, that

$$S_{dn}(E_d - E_n) + \sum_s v_{sd}S_{sn} = 0 \tag{13}$$

and, for all s,

$$S_{sn}(E_s - E_n) + v_{sd}S_{dn} = 0. \tag{14}$$

These form an infinite set of simultaneous equations, which are to be solved for the S's, furnishing thereby a series of values of E_n consistent with non-zero solutions for the S's. This problem I have solved on a previous occasion[6] on the assumption that v_{sd} did not depend on the value of the subscript s. As this assumption is too restricted for our present purposes, I will here present just a sufficient outline of the solution to show how it must be modified. From Eqs. (13) and (14) one may write

$$(E_d - E_n) - \sum_s [v_{sd}^2/(E_s - E_n)] = 0. \tag{15}$$

Now contributions to the summation in this equation will occur in two ways. There will be contributions from regions in which E_s is very different from E_n and a contribution from the region where $E_s - E_n$ is of the order of ϵ_s. If we let α_n be the least positive value of $E_s - E_n$ and set $\beta_n = \alpha_n - \epsilon_n/2$, then it may be shown (see reference 6, especially p. 755 of the earlier article) that this latter contribution is $-v_{nd}^2(\pi/\epsilon_n)$ tan $(\pi\beta_n/\epsilon_n)$, where v_{nd} is the value of v_{sd} and ϵ_n the value of ϵ_s when $E_s - E_n$ is very small. If we allow r_∞ to become very large and hence ϵ_s to become very small we may write the sum as an integral, getting

$$E_d - E_n + v_{nd}^2 \frac{\pi}{\epsilon_n} \tan \frac{\pi\beta_n}{\epsilon_n} - \int_0^\infty \frac{v_{sd}^2}{E_s - E_n} \frac{d(E_s - V_1(\infty))}{\epsilon_s} = 0, \tag{16}$$

it being understood that the singularity in the integrand is handled in such a way that no contribution to the integral results from it. This gives us the values of the perturbed energy levels. For, with any given value of E_n it allows us to find the value of β_n, and thus for any particular region we see how the perturbed levels are placed with respect to the unperturbed. It should be noted that β_n/ϵ_n approaches a definite limit for any given value of E_n as ϵ_n goes to zero.

We are really interested, however, in the absorption to the state with energy E_n, from the ground state and, indeed, for the special case in which, of the original eigenfunctions, only the one for the discrete state combines with the ground state. If this is the case, then we may take the absorption to the state E_n as proportional S_{dn}^2 and hence if we can find this quantity as a function of E_n we shall have accomplished our purpose. Now from Eq. (12), since we must have $\int \psi_n^2 d\tau = 1$ and remembering the

[7] Zener, Phys. Rev. **37**, 560 (1931). Morse and Stueckelberg, Ann. d. Physik **9**, 581 (1931). This method of handling v_{ss} avoids a troublesome difficulty previously encountered in the theory.

[8] We consider only the case in which levels of different rotational quantum number do not interact with each other and so do not need to be considered at the same time. The energy between discrete states therefore refers to the energy between two adjacent vibrational levels. See reference 6 and §3.

orthogonal properties of ψ_d and the ψ_s, we get $S_{dn}^2+\sum_s S_{sn}^2=1$. Substituting for S_{sn} from (14)

$$1=S_{dn}^2+S_{dn}^2\sum_s[v_{sd}^2/(E_s-E_n)^2]. \quad (17)$$

Now starting with the state for which E_s-E_n has the smallest positive value $E_s-E_n=\epsilon_s/2+\beta_s$, the next value of E_s-E_n is $3\epsilon_s/2+\beta_s$, etc., and similarly for $E_s<E_n$ the values run $\epsilon_s/2-\beta_s$, $3\epsilon_s/2-\beta_s$, etc. It is seen that the series can be made to converge in as small a range of E_s-E_n as we desire by making r_∞ large enough and hence ϵ_s small enough. So we can, in the limit, take v_{sd} outside the summation, as v_{nd}. The sum can be evaluated as in our former papers, and the first term becomes negligible in the limit as r_∞ goes to infinity ($\epsilon_s\to 0$). We thus find[6]

$$S_{dn}^2=\left[\frac{v_{nd}^2\pi^2}{\epsilon_n^2}\left(1+\tan^2\frac{\pi\beta_n}{\epsilon_n}\right)\right]^{-1}. \quad (18)$$

Substituting now the value of $\tan(\pi\beta_n/\epsilon_n)$ from (16) we get, finally,[9]

$$S_{dn}^2=\frac{\epsilon_n}{\pi}\left[\frac{v_{nd}^2\pi}{\epsilon_n}+\frac{\epsilon_n}{v_{nd}^2\pi}\left(E_d-E_n-\int_0^\infty\frac{v_{sd}^2}{E_s-E_n}\frac{d(E_s-V_1(\infty))}{\epsilon_s}\right)^2\right]^{-1}. \quad (19)$$

This holds, without further restriction, for the effect of a single continuum on a discrete state, the perturbations being of "intermediate size."

§2. Evaluation of the Matrix Components

The purpose of this paper is to discuss the case of special interest which arises when the two curves V_1 and V_2 cross each other as shown in Fig. 1. For the unperturbed state of the system we use the system which would be obtained if the two atoms forming the molecule exerted no force on each other,[10] then we bring in the mutual potential energy V as the perturbation energy. With this scheme V_1 and V_2 consist entirely of the terms v_{11} and v_{22}.

We shall assume in making the calculation that for the important region of r near the point

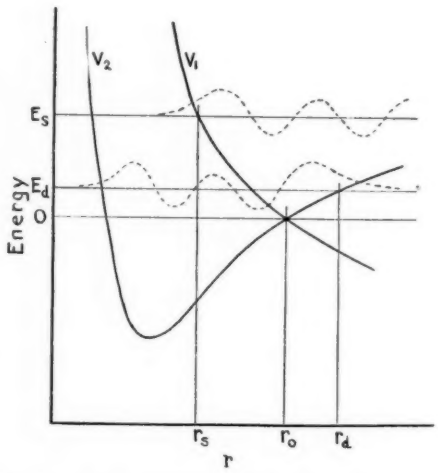

FIG. 1. Potential energy curves illustrating the situation in §2. Schematic drawings of the eigenfunction, F_d, for a discrete state of energy E_d, and the eigenfunction F_s of a continuous state with energy E_s are shown, drawn on the energy levels as zeros of ordinates. The value of v_{sd} depends on the integral of the product of F_s and F_d. It will be seen that as E_s increases and r_s thus decreases the phase relationship of F_s and F_d will change periodically and the value of v_{sd} will depend in a quasi-periodic way on r_s-r_d. See Eq. (23) and Fig. 2a (noting Eqs. (26) and (27)). The relation between v_{nd} and r_n-r_d is, of course, the same as that between v_{sd} and r_s-r_d, the subscript n here really being a special case of the subscript s. The situation depicted here does not correspond very well with the simplifying assumptions made in §2, but the position of the wave functions will roughly correspond to that producing the maximum of $A\cos(\lambda\{r_n-r_d\})$ which occurs at $\lambda(r_n-r_d)=-7$ in Fig. 2a.

[9] Dirac, Zeits. f. Physik **44**, 594 (1927) arrived at the same formula for the probability of scattering of a particle by an atom which can absorb and reemit it. It appears, in fact, that our result can be derived from Dirac's if we assume in his calculation that the particle which is reemitted is not the same one which is absorbed. Thus we could have absorption of a light particle, then predissociation (essentially equivalent to emission of another particle) the matrix component for the former process being different from the latter. If these two matrix components are different then it is no longer necessary for the matrix component for the predissociation (or reemission of the second particle) to be small (it can be of "intermediate size") which removes an apparent limitation on Dirac's derivation. I have given the other deduction here, however, in the first place because it seems interesting to look at the problem from the point of view of stationary states, in the second place because it seems worth while to have a proof which avoids the use of the Dirac δ-function. See also Weisskopf and Wigner, Zeits. f. Physik **63**, 54 (1930), especially the footnote, p. 64.

[10] This does not prevent us from bringing in the exchange phenomena in the proper way. We can also refer the electron coordinates to axes moving with the nuclei thus getting ordinary molecular states for our unperturbed states. In so doing, we bring in other perturbations due to the Coriolis forces, which may or may not be of importance.

of intersection, which we shall designate as r_0, the value of v_{12} may be taken as constant[11] and the curves V_1 and V_2 may be considered as intersecting straight lines. Under these circumstances it is possible to evaluate v_{nd} and the integral that appears in (16) and (19).

If the slope of the curve V_k at r_0 is V_k', then if the approximations indicated in the above paragraph hold good we may write for an eigenfunction[12] of the Eq. (3)

$$F_{km}=N_{km}\int_0^\infty \cos\{z^3\pm|3\eta^2V_k'|^{\frac{1}{3}}(r-r_m)z\}dz, \quad (20)$$

where

$$r_m=r_0+E_{km}/V_k' \quad (21)$$

and is the point at which $V_k=E_{km}$, as we shall let the zero point of energy be the energy of the crossing of the potential energy curves. The plus or minus sign is to be used according as V_k' is positive or negative. N_{km} is the normalizing factor.

If v_{12} is constant, and if V_1' is negative and V_2' is positive as in Fig. 1, we have

$$v_{sd}=v_{12}\int_{-\infty}^{\infty}F_sF_d dr, \quad (22)$$

the integration with respect to r being extended from ∞ to $-\infty$, which is permissible as there is but little contribution to the integral, excepting from the region between the points r_s and r_d. As shown in Appendix I this may be reduced to

$$v_{sd}=\frac{N_dN_sv_{12}\pi}{[3\eta^2(|V_1'|+|V_2'|)]^{\frac{1}{3}}}\int_0^\infty dz\cos\left\{z^3+\frac{(r_s-r_d)(3\eta^2)^{\frac{1}{3}}}{(1/|V_1'|+1/|V_2'|)^{\frac{1}{3}}}z\right\}. \quad (23)$$

The integral $\int_0^\infty dz\cos(z^3-xz)$ has been evaluated by Airy[13] over a considerable range of the parameter involved and the range may be extended by the Wentzel-Kramers-Brillouin approximation method.[14] A discussion with a table of values is given in Appendix III.

We now turn to the evaluation of

$$\int_0^\infty \frac{{v_{sd}}^2}{E_s-E_n}\frac{d(E_s-V_1(\infty))}{\epsilon_s}.$$

To a good approximation we can replace this by

$$\frac{1}{\epsilon_n}\int_{-\infty}^{\infty}\frac{{v_{sd}}^2}{E_s-E_n}d(E_s-E_n).$$

As shown in Appendix II we thus get

$$\int_0^\infty \frac{{v_{sd}}^2}{E_s-E_n}\frac{d(E_s-V_1(\infty))}{\epsilon_s}=B_n\int_0^\infty dz\cos\{z^3+\lambda(r_n-r_d)z\}\int_0^\infty dt\sin\{t^3+\lambda(r_n-r_d)t\} \quad (24)$$

where

$$B_n=\pi^3{v_{12}}^2{N_d}^2{N_n}^2{\epsilon_n}^{-1}(3\eta^2)^{-\frac{1}{3}}(|V_1'|+|V_2'|)^{-\frac{1}{3}} \quad (25)$$

and

$$\lambda=(3\eta^2)^{\frac{1}{3}}(1/|V_1'|+1/|V_2'|)^{-\frac{1}{3}}, \quad (26)$$

r_n being equal to r_0+E_n/V_1'. The evaluation of the second integral in (24) is discussed in Appendix III. If we also write

$$\int_0^\infty \cos(z^3+xz)dz=A_{\cos}(x) \quad (27)$$

[11] This is similar to the assumption commonly made in calculating the absorption intensities in band spectra.

[12] See Watson, *Bessel Functions*, Cambridge, 1922, p. 188. This solution of Eq. (3) has the general properties of an eigenfunction, inasmuch as it becomes small when r becomes small, and while it does not actually become zero for $r=0$, it is a sufficiently good approximation. F_{km} has the form (20), of course, only in that region where the potential curve is approximately a straight line.

For the continuous curve the energy must be determined by the boundary condition at r_∞, and the normalizing factor is determined by the way this form joins on to the asymptotic form of F_{km} (that is, F_s, in this case). The amplitude of the wave for large values of r is fixed by Eq. (7), and is the same for all energies. If the wave-length is short enough the value of N_s which gives the amplitude near r_0 will vary from one value of E_s to another as $(E_s-V_1(\infty))^{\frac{1}{4}}$. See, e.g., Nordheim, Zeits. f. Physik **46**, 842 (1927).

[13] Airy, Trans. Camb. Phil. Soc. **8**, 598 (1848).

[14] See Kramers, Zeits. f. Physik **39**, 828 (1926).

and
$$\int_0^\infty \sin(z^3+xz)dz = A_{\sin}(x), \tag{28}$$

then,[15] from (19), (23) and (24),

$$S_{dn}^2 = \left(\frac{\pi B_n}{\epsilon_n}\right)^{-1}\left[A_{\cos}^2(\lambda\{r_n-r_d\})+\left(\frac{(E_d-E_n)/B_n - A_{\cos}(\lambda\{r_n-r_d\})A_{\sin}(\lambda\{r_n-r_d\})}{A_{\cos}(\lambda\{r_n-r_d\})}\right)^2\right]^{-1}. \tag{29}$$

This expression gives the absorption coefficient of the single broadened, shifted, and distorted predissociation line whose unperturbed energy is $E_d(=V_2'(r_d-r_0)$ by (21)) as a function of the total energy $E_n(=V_1'(r_n-r_0)$ by (21)) of the energy level which is the final state in the absorption process.

The best way to appreciate the behavior of S_{dn}^2 is to study a few concrete examples. S_{dn}^2, it is to be remembered, is a function of E_n, since E_d is a perfectly definite energy for any discrete line; S_{dn}^2 plotted as a function of E_n will give the shape of the broadened discrete line. Let us now consider what happens when E_d has such a value that when $E_d=E_n$ we have $A_{\cos}(\lambda\{r_n-r_d\})$ at its first* zero point. To distinguish this special case we shall designate this value of E_d as E_{d_0}. In Fig. 2(b) we have plotted $S_{d_0n}^2$ as a function

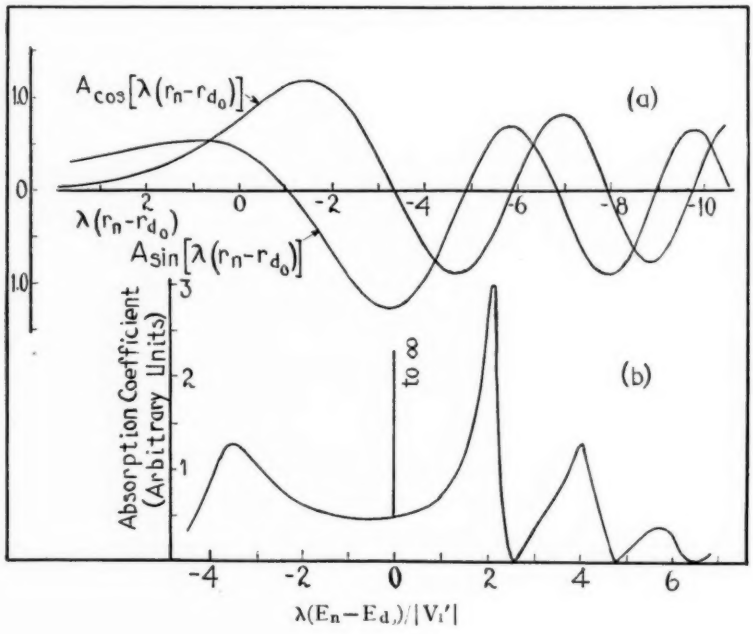

FIG. 2.

of $\lambda(E_n-E_{d_0})/V_1'$, the increments of which, it will be observed, are equal to the increments of $\lambda(r_n-r_d)$. We take $-5V_1'/\lambda$ as the value of B_n. The ordinates are in arbitrary units. Just above the curve for $S_{d_0n}^2$ we have plotted $A_{\cos}(\lambda\{r_n-r_{d_0}\})$ and $A_{\sin}(\lambda\{r_n-r_{d_0}\})$ against $\lambda(r_n-r_{d_0})$ in such a position as to bring out the relationship between the various curves. Now suppose we consider another case in which E_d has a value somewhat displaced from its former value. Then the point at which $E_n=E_d$ is removed by a certain amount from the value of E_n for which $A_{\cos}(\lambda\{r_n-r_d)=0$, and this is

[15] In the evaluation of this expression we note that B_n is approximately independent of E_n. See Eq. (6) and reference 12.

* The general features of the phenomena will be the same for any zero point.

different than the amount by which E_d is different from E_{d_0}. The latter quantity is, of course, equal to $E_d-E_{d_0}$, while the former is equal to $(E_d-E_{d_0})(|V_1'|+|V_2'|)/|V_2'|$. For the value of E_n where $A_{\cos}(\lambda\{r_n-r_d\})$ is zero is $E_{d_0}-(E_d-E_{d_0})|V_1'|/|V_2'|$, this being the point, as is readily verified, where r_n-r_d equals the original zero-point value of $r_n-r_{d_0}$. Several intensity curves, as they appear in the immediate neighborhood of the energy for which $A_{\cos}(\lambda\{r_n-r_d\})=0$ are exhibited in Fig. 3. These curves are based on the assumption that $|V_1'|=|V_2'|$, and again B_n is taken as $-5V_1'/\lambda$. The maximum in each case corresponds to the infinitely intense and narrow line of Fig. 2, now displaced and broadened. Thus we see that the apparent position of the discrete line will, unless the line happens to be in the special position, E_{d_0}, be displaced toward the zero-point for $A_{\cos}(\lambda\{r_n-r_d\})$ by an amount ΔE_d, where

$$\Delta E_d \leq (E_d-E_{d_0})(|V_1'|+|V_2'|)/|V_2'|, \quad (30)$$

the equality sign occurring for $B_n=\infty$. If E_d is not too greatly different from E_{d_0} the rest of the intensity curve will not differ greatly from the curve in Fig. 1 except that it will be displaced by the same amount that the zero point of $A_{\cos}(\lambda\{r_n-r_d\})$ is displaced, i.e., by an amount $-(E_d-E_{d_0})|V_1'|/|V_2'|$. As the value of $E_d-E_{d_0}$ grows greater the adjacent intensity maximum develops while the maximum near E_{d_0} grows smaller. When $E_d-E_{d_0}$ has such a value that $|A_{\cos}(\lambda\{r_n-r_d\})|$ for $E_n=E_d$ is near its maximum then both maxima in the intensity curve will be approximately of equal size.

It is interesting to consider a little further the behavior of the expression (29) when the line is so narrow (as is actually practically the case in Fig. 3) that $A_{\cos}(\lambda\{r_n-r_d\})$ and $A_{\sin}(\lambda\{r_n-r_d\})$

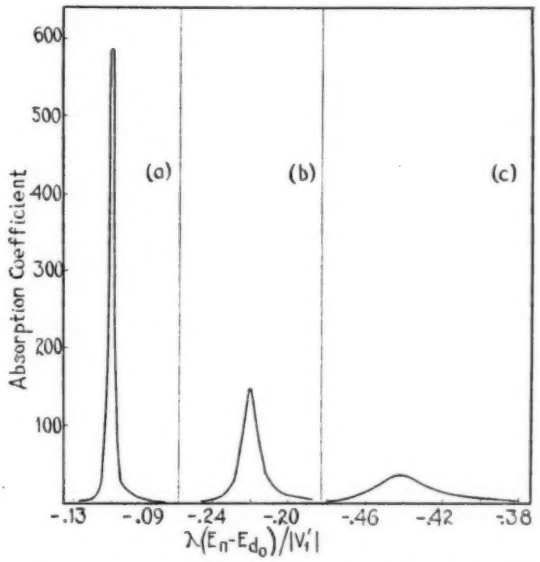

FIG. 3. The broadened predissociation line in various cases. (a) $\lambda(E_d-E_{d_0})/|V_1'|=0.15$; (b) $\lambda(E_d-E_{d_0})/|V_1'|=0.3$; (c) $\lambda(E_d-E_{d_0})/|V_1'|=0.6$. Units for the absorption coefficient arbitrary but same as in Fig. 2b.

are nearly constant over the width of the line. Then the energy $E_n(\max)$ at which the absorption coefficient has a maximum is given very closely by

$$(E_d-E_n(\max))/B_n-A_{\cos}(\lambda\{r_n(\max)-r_d\})A_{\sin}(\lambda\{r_n(\max)-r_d\})=0 \quad (31)$$

and the half absorption width ΔE_n of the line will be given by

$$\Delta E_n=2B_nA_{\cos}^2(\lambda\{r_n(\max)-r_d\}) \quad (32)$$

as may be readily seen from (29) by subtracting the one value of E_n where S_{dn}^2 has half its maximum value from the other. Now we have already noted that if B_n increases (for example by increasing v_{12}) $E_n(\max)$ tends to go to such values that $A_{\cos}(\lambda\{r_n(\max)-r_d\})$ approaches zero. It is readily seen why this happens from (31). As this happens $E_d-E_n(\max)$ tends to approach a constant value, in terms of which, B_n and $A_{\sin}(\lambda\{r_n(\max)-r_d\})$ it is possible to evaluate $A_{\cos}(\lambda\{r_n(\max)-r_d\})$ from (31). $A_{\sin}(\lambda\{r_n(\max)-r_d\})$ also tends to approach a constant value as B_n increases. From (31) and (32) we have

$$\Delta E_n=\frac{2(E_d-E_n(\max))^2}{B_nA_{\sin}^2(\lambda\{r_n(\max)-r_d\})}.$$

One thus arrives at the curious result that the larger B_n and hence the perturbation matrix component v_{12} the sharper is the displaced discrete line, though at the same time its intensity decreases, as is readily seen from (29). It is a little difficult to see at just what point

this breaks down. Since the width of the lines becomes smaller as B_n increases, it would at first sight seem that our criterion that two discrete lines should not be so broadened as to overlap appreciably would be automatically fulfilled. But the secondary structure of Fig. 2 must be included in the breadth of any discrete line. As B_n increases the secondary structure increases in prominence, the secondary maxima becoming stronger and narrower, and as soon as the secondary structure of an adjoining discrete line becomes as important in the neighborhood of that discrete line itself the calculation must of necessity break down. It is by no means certain, however, that this criterion for the validity of the treatment used is stringent enough.

It should be stated that the spacing between the secondary maxima will quite often or perhaps usually be of the same order of magnitude as the spacing between adjacent vibrational levels, which means that the secondary maxima will probably not be of importance in practical spectroscopy, though we conjecture they may have something to do with the phenomena in iodine chloride, as mentioned in §4.

It is interesting to note that the spacing of the maxima of the secondary structure is closely related to what the spacing of energy levels of the upper adiabatic, non-crossing curve would be if it were the unperturbed curve, but the nature of the wave functions is different, and the phenomena involved could be properly understood only if the effect of all the discrete states could be studied.

§3. Vibration-Rotation Levels of a Molecule

The actual appearance of the term diagram of a diatomic molecule, to be expected on the basis of the theory presented, can be readily deduced from the above discussion. The theory is based on the assumption that a discrete energy level interacts with only one continuum; consequently it can be applied only to molecules in which there is a selection rule operating,[16] such that a discrete state with given rotational quantum numbers interacts only with continuous states with the same rotational quantum numbers.

If the rotational quantum number (for total angular momentum) is J, then in order to get the proper effective potential energy curve we must add to both V_1 and V_2 the quantity $J(J+1)/\eta^2 r^2$. Thus the point, r_0, of intersection of the potential energy curves is independent of J, but the energy of intersection is increased over that for $J=0$ by an amount $J(J+1)/\eta^2 r_0^2$. For our present purposes we may ignore the change of slope of V_1 and V_2 in the neighborhood of r_0 and assume that the curves are corrected simply by adding the amount $J(J+1)/\eta^2 r_0^2$.

Suppose a given rotational line is at such a position that $A_{\cos}(\lambda\{r_n - r_d\}) = 0$ when $E_n = E_d$. Then the line with the next higher value of J will have an energy such that when $E_n = E_d$ the quantity $A_{\cos}(\lambda\{r_n - r_d\})$ is not equal to zero; for, in general, $r_e \neq r_0$, where r_e is the value of r at the minimum of the potential curve, and the energy of the line increases at a different rate than the energy for the crossing point r_0. Thus in the molecule we will have one rotation level sharp, and it will be surrounded on either side by levels growing more and more diffuse. The diffuse levels will be displaced in position, and it may be readily verified that if $r_e < r_0$ the spacing between levels will be less than normal; in fact, one could even have reversal of the order, the levels of lower rotational quantum number having higher energy.

§4. Application to Iodine Chloride

We shall now consider, in the light of the theory just developed, the rather complex set of predissociation phenomena which has been found by Brown and Gibson[2] by examination of the absorption spectrum of iodine chloride.

In describing these phenomena we shall follow, as far as possible, the standard notation used by Brown and Gibson. v'' and v' will be the re-

[16] In general such a selection rule will operate, at least if Hund's Case a holds. For the value of J and its projection on a given axis must be the same for the two states which interact, the only ambiguity remaining, with given potential energy curves, after J and its projection have been determined, being the orientation of the spin in one direction or the other referred to J, which gives rise to Λ-type doubling. But there will be a selection rule for the spins which prevent the two states due to Λ-type doubling from both interacting, at least appreciably, with any one state belonging to the other potential energy curve.

spective vibrational quantum numbers and J'' and J' the respective rotational quantum numbers of the initial and final states giving rise to an absorption line. $B_{v'}$ will be used for the quantity $h^2/8\pi^2 I_{v'}$ where $I_{v'}$ is the moment of inertia for the v' vibrational level. Brown and Gibson have given their results in the form of wave numbers of observed lines. As we shall be chiefly interested in energy levels, all values here given, unless otherwise noted, are values of energy levels, obtained from the observed spectral lines by taking into account the energy of the initial states; the values are in wave numbers (cm^{-1}) and are referred to the state, $v''=1$, $J''=0$, as the zero of energy. $\nu_{v'}$ will denote the energy of the band head, quantum number v', r will denote the distance between atoms, and r_e the equilibrium distance for the excited ($'$) energy level.

Brown and Gibson have found a number of bands corresponding to an absorption $^3\Pi_0 \leftarrow {}^1\Sigma$, which they have designated as System II. They have measured the positions of a number of band-heads, analyzed the rotational structure in so far as possible, determined v' values by use of the isotope effect and given an estimate of the convergence limit. They have found that the higher members of the band show predissociation phenomena. Their results are summarized in Table I. The data for $v'=1$, 2 and 3 are obtained directly, whereas that for $v'=4$, I have obtained by indirect means to be described.

TABLE I. *Constants for bands of system II.*

v'	$\nu_{v'}(cm^{-1})$	$B_{v'}$*	Remarks
1	17,093		Lines sharp
2	17,282.5	0.0829	Lines sharp
3	17,446.3	0.0800	Lines sharp $J \lesssim 50$, diffuse $J \gtrsim 50$
4	17,580	0.0748	Most lines diffuse
Convergence	17,864		See Brown and Gibson, p. 537

* $B_{v'}$ is in such units that energies will be obtained in cm^{-1}.

No regular band-heads or band structure are observed for $v'=4$ or greater. Instead there are isolated groups of diffuse and sharp lines, which come in pairs, the pairing being due to the fact that there are P and R branches present. Each group consists of a central sharp line, surrounded by others of increasing diffuseness as one goes away from the sharp central lines. The lines of three such groups have been measured and by use of the combination differences their rotational quantum numbers have been obtained. In addition, there is a background consisting of a series of very faint diffuse absorption maxima which are referred to as System III. The superficial resemblance of these phenomena to those considered in §§2 and 3, is at once apparent. The groups of lines presumably correspond to lines such as shown in Fig. 3, while, though this is more doubtful, one may suppose that the faint maxima correspond to the maxima of Fig. 2b; there would possibly be enough states piled together at a band head to make these visible.[17]

Brown found by his analysis that the sharp energy levels of the two most prominent groups of sharp and diffuse lines, which were designated as Series I and Series II, had rotational quantum numbers J' equal to 28 and 46, respectively. Both Series I and Series II presumably have $v''=1$, $v'=4$. Now with any reasonable slopes for the two curves V_1 and V_2 it is utterly impossible to account for two sharp energy levels appearing so close together, the periodicity given by the theory being of a different order of mag-

[17] Brown had a tentative explanation of these predissociation phenomena. He noted that the faint maxima seemed to be arranged as though they were an independent series of band-heads, which he called System III. The potential energy curve for these band-heads he supposed to be the adiabatic curve formed by the crossing of a repulsive curve and the curve of System II. He supposed the sharp lines to belong at the same time to System III and System II, as their placing seemed to allow that assumption. He supposed the spacing of the lines to be that characteristic of the rotational levels of System III. From this he was able to get an apparent position of the minimum of the potential curve for System III, and the approximate point at which it was crossed by the potential curve. Van Vleck, however (see Brown and Gibson, p. 542) preferred to consider the sharp lines as vestigial remains of System II, which is more in accord with the view we take here. One obvious objection to any literal acceptance of Brown's ideas and one which he apparently did not realize existed, is the fact that the crossing of the curves occurs at a point (see Brown and Gibson's Fig. 4) which is nowhere near the Morse curve for System II. (See our Fig. 4 and reference 22.) It must be admitted that our theory runs into a somewhat similar, but I believe less pronounced difficulty. In any event, Brown's suggestion, while containing a certain element of truth, had no absolute theoretical significance, as he himself well realized.

nitude. It is also apparently impossible to account for the phenomena by changing the vibrational numbering assuming, e.g., that $v''=2$ for one of the sharp lines and its surrounding group of diffuse lines, as this pushes the energy level beyond the dissociation limit of the group of bands, which appears from the analysis to be pretty well fixed. The only reasonable explanation I have been able to find lies in assuming that we have here a new and very curious kind of isotope effect, namely that Series II is due to the isotopic molecule[18] ICl^{37}. If this assumption is made, it is necessary to compare the combination differences ($\Delta_2 F''$) with the combination differences for the molecule ICl^{37}. These can be found from those given in Table I of Brown and Gibson's paper by a short extrapolation, and a correction to take into account the difference in reduced mass. It is found that the agreement between the expected combination differences and those actually observed is good[19] if one assigns to the sharp line the value $J'=48$ instead of 46. Since one knows that the value of $B_{v''}$ for $v''=1$ for the ICl^{35} molecule is 0.1132 and the value for $B_{v''}$ for the ICl^{37} molecule is, therefore, very approximately equal to 0.9576×0.1132 or 0.1084 (the value 0.9576 being the ratio of the reduced mass of ICl^{35} to that of ICl^{37}) one can, from the data given by Brown and Gibson, calculate the actual energies of the sharp and diffuse levels by adding to the observed frequency the proper value, $B_{v''}J''(J''+1)$, and, in the case of Series II, subtracting 12.36, to allow for the isotope displacement of the lower band-head.[20] This will give the energy referred to the $J''=0$ level of the $v''=1$ vibrational level. In most cases two values for a given energy have been obtained, and the average of the two has been used. The results of this calculation have been tabulated in the second column of Table II. If now we assume the sharp line to be unshifted in position, we can calculate the unperturbed energy $\nu_{v'}$ for $v'=4$, provided we can make an estimate of $B_{v'}$. From the values of the latter quantity for $v'=2$ and $v'=3$, I estimate that for $v'=4$ it will be about 0.0765 for ICl^{35} and this will give 0.0733 for ICl^{37}, neglecting the effect of the isotope shift of the band-head. We thus find for $v'=4$, $J'=0$, ICl^{35} the value 17,580.3 cm^{-1} and for $v'=4$, $J'=0$, ICl^{37} the value 17,566.2 cm^{-1} giving an isotope shift of -14.1. We can calculate the isotope shift from the formula $\omega_{v'}(\rho-1)(v'+\frac{1}{2})$ where $\omega_{v'}$ is the frequency of the v' vibrational level and $\rho-1=(M_{35}-M_{37})/(M_{35}+M_{37})$ the M's being the reduced masses. $\omega_{v'}$, judging from Table I, is about 120. This gives for the isotope shift -11.7. The discrepancy would be increased a little by taking into account the effect of the displacement of the ICl^{37} band-head on $B_{v'}$ for this isotope, as this would tend to increase $B_{v'}$

TABLE II. *Energy levels for series I and II and calculation of* $\Delta E_d/(E_d-E_{d_0})$.

Series I, $J'=25$–32, series II, $J'=46$–50.

J'	Energy (cm^{-1})	Obs. displ. (cm^{-1})	ΔE_d (cm^{-1})	$E_d-E_{d_0}$ (cm^{-1})	$\frac{\Delta E_d}{(E_d-E_{d_0})}-1$
25*uu*	17,634.26	−8.18	3.94	1.325	1.97
26*uu*	636.98	−5.46	2.77	0.900	2.08
27	639.62	−2.82	1.37	0.458	1.99
28*s*	642.44	0.			
29	645.48	3.04	−1.30	0.474	1.74
30*u*	648.70	6.26	−2.57	0.965	1.66
31*uu*	652.08	9.64	−3.82	1.47	1.60
32	655.66	13.22	−5.03	2.00	1.52
46*uu*	17,729.35	−8.99	5.22	1.55	2.37
47*u*	733.82	−4.52	2.66	0.785	2.39
48*s*	738.34	0.			
49*u*	742.99	4.65	−2.68	0.802	2.34
50*uu*	747.96	9.62	−5.19	1.62	2.20

s = sharp, *u* = broad, *uu* = very broad.

[18] This conclusion depends of course on all the assumptions we have made. It is not claimed that we have here made an exhaustive analysis, but certain support is lent by other observations. Thus Brown and Gibson state, p. 536, that it was impossible to observe the isotope shift of Series I and II, from which we may infer that no ordinary isotope effect is to be found. And I am indebted to Professor Gibson for the information that the intensity of the lines of Series I is stronger than that of the lines of Series II, and that judging by eye they might easily be in the isotope ratio. Of course, the Boltzmann factor would tend to make Series II weaker than Series I, but this should be about compensated by the increasing multiplicity of the lines with larger J values.

[19] This is also indicated by the fact that when one calculates the energy of rotational lines from the P and R lines using the value of $B_{v''}$ for the molecule ICl^{37} one gets values which agree with each other in all cases to within 0.04 cm^{-1}.

[20] I cannot check the value of 12.19 given by Brown and Gibson, but the difference is not of much significance.

a little; nevertheless, the agreement seems to be reasonably good, considering the uncertainties involved. Thus if we used the, to be sure, rather low value of $B_{v'}=0.073$ for ICl^{35}, to which Brown was actually led by the assumption that both groups of lines belonged to ICl^{35}, we get for the isotope shift -9.3, already on the other side of the calculated value. The value for $B_{v'}$ which I have tabulated in Table I lies between these extremes. And it must not be forgotten that the assumption, which we have made (and which Brown also made), that the sharp lines are unshifted in position, is based on the approximate calculations of §2; but it is, in any event, probably safe to assume that the two sharp levels are displaced approximately the same amount, which would leave the isotope displacement the same.

If, however, we continue to assume that the lines are unshifted, we are now in a position to calculate the value of r which we have called r_0 at which the intersection of the two potential energy curves occurs. For it seems probable that the sharp line in *each* case corresponds roughly to the *first* zero* in $A_{\cos}(\lambda\{r_{n_d}-r_d\})$, where $E_{n_d}=E_d$. If this is so, then the energy of the sharp level of Series I, minus the energy of the intersection of the potential curves should be equal to the same quantity for the sharp level of Series II. The energy of intersection will be the same for the two isotopes for $J'=0$, but needs to be corrected for given values of J' by an amount $J'(J'+1)B_i$ where $B_i=h^2/8\pi^2Mr_0^2$ and is different for the two isotopes. If we let B_i be the value for the molecule ICl^{35}, then the difference in the correction for the two cases will be $48\times49\times0.958\,B_i-28\times29\,B_i$, and this must be equal to the difference in energy of the two sharp levels, which is 95.9. We thus find that $B_i=0.0666$ and $r_0=3.03$.

We can derive some further information on the assumption that the sharp levels of Series I and Series II correspond to the first zeros of $A_{\cos}(\lambda\{r_{n_d}-r_d\})$ for the respective isotopic molecules. The energy for the level $J'=28$ is 17,642.4 cm^{-1} and when corrected by the subtraction of the amount $J'(J'+1)B_i$ or $28\times29\times0.0666$ it becomes 17,588.4. Now Brown states that in the $v'=3$ band the rotation levels can be followed up to about $J'=52$ and in this neighborhood the levels gradually become diffuse. It is difficult to get any comparison between the breadth of these levels and those of Series I and II from Brown and Gibson's paper. Likewise, it is difficult to know the values of $A_{\cos}(\lambda\{r_n(\max)-r_d\})$ for the individual levels of Series I and II. If these two pieces of information were at hand we would be able, from (32), to get $A_{\cos}(\lambda\{r_n(\max)-r_d\})$ and hence $\lambda\{r_n(\max)-r_d\}$ for the $v'=3$, $J'=52$ level. I make the assumption that the broadening of the level at $v'=3$, $J'=52$ is about the same as that of the broadest of the lines of Series I and II yet visible, and it seems quite likely that $A_{\cos}(\lambda\{r_n(\max)-r_d\})$ is still quite small for all the lines of Series I and II. The value of $A_{\cos}(\lambda\{r_n-r_d\})$ has become pretty small for $\lambda(r_n-r_d)=4$ and we take this as the value of $\lambda\{r_n(\max)-r_d\}$ for $v'=3$, $J'=52$. This would make the range $\Delta\lambda(r_n(\max)-r_d)$ of the quantity $\lambda(r_n(\max)-r_d)$ between the level $v'=3$, $J'=52$ and the first sharp line of Series I or II equal to about 7.5. Now the energy of $v'=3$, $J'=52$ can be calculated by adding the quantity $J'(J'+1)B_{v'}$ to the energy of the band head; it must then be corrected by subtracting $J'(J'+1)B_i$; the final result is 17,483.2 cm^{-1}. Therefore the range $\lambda(r_n(\max)-r_d)=4$ to $\lambda(r_n(\max)-r_d)=-3.5$ corresponds to a range in energy of about 17,483 to 17,588 cm^{-1}. Now since $r_n=r_0+E_n/V_1'$ and $r_d=r_0+E_d/V_2'$ we can calculate the quantity $1/|V_1'|+1/|V_2'|$ from the relation $\Delta\lambda(r_n(\max)-r_d)=7.5$, using Eq. (26), and putting in the numerical values.[21] We thus find $1/|V_1'|+1/|V_2'|=0.0086$. The units of V_1' and V_2' are cm^{-1} per A. Since the slope of the Morse curve[22] for V_2 is around 1200 cm^{-1} per A in the neighborhood of the crossing point of the potential energy curves, it is seen that this gives for V_1' a value of about -125 cm^{-1} per A. Since the atomic levels of iodine and chlorine are such that

* This amounts to saying that in the case of each isotope the unperturbed energy of the sharp line corresponds to the energy we have called E_{d_0} in §2.

[21] E_d can, in each case, be taken as equal to E_n (max) for these purposes. Remember, also, V_1' and V_2' have opposite signs.

[22] Morse, Phys. Rev. **34**, 57 (1929). The Morse curve for V_2 constructed from the data of Table I is given by the expression $V_2=16{,}758+1106(1-e^{-4.70(r-r_e)})^2$ and is shown in Fig. 4. The value of r_e, calculated by extrapolation of the $B_{v'}$ values with the aid of the work of Dunham, Phys. Rev. **41**, 721 (1932), is found to be 2.62A.

the curve V_1 must be approaching an asymptotic value some 500 cm^{-1} less than the energy of intersection,[23] it appears that this value is rather unreasonably small.

A rather more serious difficulty appears when we attempt to use Eq. (30) to obtain the value of $|V_1'|/|V_2'|$. For the value found is inconsistent with the above conclusion. This is shown in Table II. In compiling this table we have taken the energy of the sharp level as E_{d_0} in both Series I and Series II. In Column 3 is given the observed difference of energy between the given level and the sharp level (Obs. Displ.) and in Column 4 is given ΔE_d which is obtained from Column 3 by subtracting from it $[J'(J'+1) - J_0(J_0+1)]B_{v'}$, where J_0 is the J' value for the sharp level, this being the expected difference in energy if the lines were not displaced. To get $E_d - E_{d_0}$, corrected for the change in energy of the point of intersection, we may use the obvious relation

$$E_d - E_{d_0} = [J'(J'+1) - J_0(J_0+1)](B_{v'} - B_i);$$

the value of $E_d - E_{d_0}$ is given in Column 5. Column 6 gives the value of $\Delta E_d/(E_d - E_{d_0}) - 1$ which from (30) is a minimum value for $|V_1'|/|V_2'|$. This turns out not to be quite constant, but this lack of constancy would seem to be a comparatively minor difficulty. The difference in the values of this ratio for Series I and Series II may be due to the actual difference in this ratio due to the change in slope of the curves V_1 and V_2 when the rotational term is added. In making the calculations of Table II I have used the values $B_{v'} = 0.0748$ and $B_i = 0.0666$, ICl^{35}, with the corresponding values for ICl^{37}. The value of $B_{v'}$ is chosen so as to make the isotope effect for the vibration level $v' = 4$ come out about right.

In seeking to explain the discrepancies between the values of $|V_1'|/|V_2'|$ calculated in different ways, a number of possibilities come to mind. In the first place, it may be that the curve V_2 begins to deviate somewhat from a Morse curve around $v' = 4$, and has a somewhat smaller slope. This is suggested by the low value of $B_{v'}$ for $v' = 4$, and the rather low energy of the band-head which we have found, in spite of the fact that the values of $B_{v'}$ for $v' = 2$ and 3 have just about the relation to each other that one might expect for a Morse curve.[24] It should be borne in mind that rather sudden changes can occur in the law of force between two atoms in a given electronic state, and this, in fact, is known to occur in another potential energy curve[25] of ICl. It hardly appears, however, that we can account in this way for all of the discrepancy, though it might be part of the explanation. Another possible factor is a breaking down of the assumptions that v_{12} is independent of r, and that the curves can be taken as straight lines near the point of intersection. Thus one would expect the value of V_1' as determined in Table II to be rather the value of V_1' at an energy near E_d, while the other method of determining V_1' might be expected to give a sort of average value between the point of intersection and E_d. So if the curve V_1 were quite flat in the neighborhood of the point of intersection and then bent up rather suddenly at somewhat smaller values of r, as in Fig. 4, this might produce the effect observed. Or possibly the flat curve V_1 intersects the other

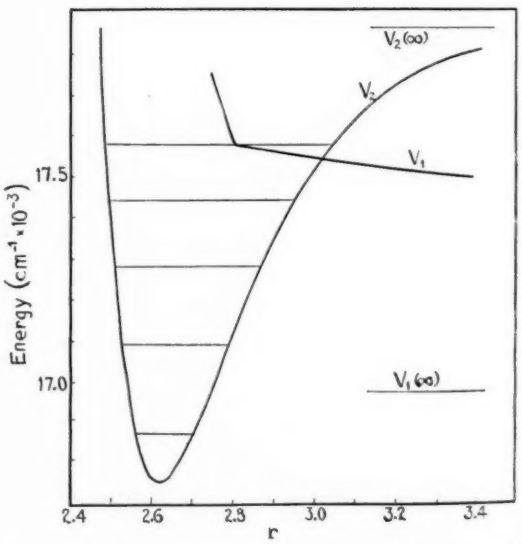

FIG. 4. Morse curve and hypothetical repulsive curve for iodine chloride.

[23] This is shown in Fig. 4. See Brown and Gibson, p. 537.

[24] The value of r_0 is also about what one might expect from the Morse curve, but it may well be too small, due to the approximations we have made in calculating it.

[25] Curtis and Darbyshire, Trans. Faraday Soc. **27**, 85 (1931).

side of the curve V_2. This would certainly produce complications of an unpredictable sort. It is also possible that the assumption that only one discrete energy level need be considered at a time is not quite correct. Finally, it is not at all certain but that we would do better in this instance if we used the adiabatic non-crossing curves to define our unperturbed states rather than the crossing curves. An attempt will be made to find approximate solutions, using the adiabatic curves as the unperturbed curves, in order to see whether this assumption fits in better with the iodine chloride data.

Before concluding, mention should be made of certain other sharp and diffuse lines which do not go with the regular bands and which do not belong to Series I or II. Particularly noticeable is another group of lines called Series III by Brown and Gibson for which apparently $v'=5$, and which is remarkable in that it contains many more lines than Series I or Series II. It does not seem to be worth while to attempt any detailed discussion of Series III.

We have already noted the existence of faint absorption maxima in the same region of the spectrum as Series I or Series II, and have stated that it is tempting to suppose that they have something to do with the secondary maxima of Fig. 2b. It must be said however that their spacing is much closer than would be expected. One of these diffuse maxima, which occurs at 17,577 cm^{-1}, Brown and Gibson identify with the band-head for the $v'=4$, $v''=1$ band. This however, does not seem reasonable, as from Table II we may judge that the head of this band would be displaced to around 17,600.

In conclusion, I think it may be said that while it does not seem possible to account quantitatively for the predissociation phenomena in iodine chloride, progress has been made in understanding and interpreting them, and affording a basis for their discussion.

Appendix I—Evaluation of Integral, Eq. (22)

If we denote the quantity $|3\eta^2 V_k'|^{\frac{1}{3}}$ by C_k, then we may write from (20) (omitting the normalizing factors)

$$\int_{-\infty}^{\infty} F_s F_d dr = \int_{-\infty}^{\infty} dr \int_0^{\infty} dz \int_0^{\infty} dt \cos [z^3 - C_1(r-r_s)z] \cos [t^3 + C_2(r-r_d)t].$$

We may extend the integrations with respect to z and t from $-\infty$ to ∞, providing we divide through twice by 2. Doing this, and making a double application of Formula 596 of Peirce's *Short Table of Integrals*, the expression becomes

$$\tfrac{1}{4}\int_{-\infty}^{\infty} dr \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dt \{\cos [(C_2 t - C_1 z)r] \cos [z^3 + t^3 + C_1 r_s z - C_2 r_d t] + \tfrac{1}{2} \cos [z^3 - t^3 - C_1 r z + C_1 r_s z - C_2 r t + C_2 r_d t] - \tfrac{1}{2} \cos [z^3 + t^3 + C_1 r_s z - C_2 r_d t - C_2 r t + C_1 r z]\}.$$

It may be readily seen, by substituting $-t$ for t and $-r$ for r in one of them, that the last two terms cancel in the integration. We now perform the integration with respect to r, but instead of integrating from $-\infty$ to ∞, which gives an indeterminate result, we integrate between very large but arbitrary limits, let us say[26] $-r_1$ and r_1. This gives us

$$\tfrac{1}{2}\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dt (C_2 t - C_1 z)^{-1} \sin [(C_2 t - C_1 z) r_1] \cos (z^3 + t^3 + C_1 r_s z - C_2 r_d t).$$

We now change over to the variables $C_2 t - C_1 z$ and $t+z$. The Jacobian of this transformation is $1/(C_1+C_2)$. If we integrate with respect to $C_2 t - C_1 z$, holding $t+z$ constant, it will be noted that if r_1 is great enough all the contribution to the integral will come from the point where $C_2 t - C_1 z$ is zero. We can thus use the known formula $\int_{-\infty}^{\infty} x^{-1} \sin mx\, dx = \pi$, setting the variables in the cosine function equal to the values they have at $C_2 t - C_1 z = 0$. If we let $t+z=y$, then, when $C_2 t - C_1 z = 0$, we have $z^3 + t^3 + C_1 r_s z - C_2 r_d t = y^3 (C_1^3 + C_2^3)(C_1+C_2)^{-3} + y(r_s - r_d) C_1 C_2 (C_1+C_2)^{-1}$. If we make the further substitution $s^3 = y^3 (C_1^3 + C_2^3)(C_1+C_2)^{-3}$, we get for the final value of the integral (remembering the integrand must be multiplied by the Jacobian of the transformation)

$$\pi 2^{-1} (C_1^3 + C_2^3)^{-\frac{1}{3}} \int_{-\infty}^{\infty} ds \cos [s^3 + s C_1 C_2 (r_s - r_d)(C_1^3 + C_2^3)^{-\frac{1}{3}}]$$

which substituted into (22) gives an expression which may readily be seen to be equivalent to (23).

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[26] It is convenient, but by no means necessary, to have the positive and negative limits the same.

Appendix II—Evaluation of Integral, Eq. (24)

We make the substitution $r_n-r_s=x$, and use the definition of λ (Eq. 26). It is seen that $(E_s-E_n)^{-1}d(E_s-E_n)=dx/x$ and substituting from (23) into the left-hand side of (24) we have for the integral (omitting the constant factor from the portion of (23) in front of the integral sign)

$$\int_0^\infty dz\int_0^\infty dt\int_{-\infty}^\infty dx\, x^{-1}\cos\left[z^3-\lambda xz+\lambda(r_n-r_d)z\right]\cos\left[t^3-\lambda xt+\lambda(r_n-r_d)t\right].$$

A trigonometric transformation gives

$$\tfrac{1}{2}\int_0^\infty dz\int_0^\infty dt\int_{-\infty}^\infty dx\, x^{-1}\cos\left[z^3+t^3+\lambda(r_n-r_d)(z+t)-\lambda x(z+t)\right]+\cos\left[z^3-t^3+\lambda(r_n-r_d)(z-t)-\lambda x(z-t)\right]$$
$$=\tfrac{1}{2}\int_0^\infty dz\int_{-\infty}^\infty dt\int_{-\infty}^\infty dx\, x^{-1}\cos\left[z^3+t^3+\lambda(r_n-r_d)(z+t)-\lambda x(z+t)\right].$$

Another trigonometric transformation gives

$$\tfrac{1}{2}\int_0^\infty dz\int_{-\infty}^\infty dt\int_{-\infty}^\infty dx\, x^{-1}\cos\left[z^3+t^3+\lambda(r_n-r_d)(z+t)\right]\cos\left[\lambda x(z+t)\right]+\sin\left[z^3+t^3+\lambda(r_n-r_d)(z+t)\right]\sin\left[\lambda x(z+t)\right],$$

which may be readily integrated, yielding $(\pi/2)\int_0^\infty dz\int_{-\infty}^\infty dt\sin\left[z^3+t^3+\lambda(r_n-r_d)(z+t)\right]$. When the integrand is expanded as the sine of the sum of two angles, $z^3+\lambda(r_n-r_d)z$ and $t^3+\lambda(r_n-r_d)t$, it yields one term which vanishes in the integration because the integration from 0 to ∞ cancels that from $-\infty$ to 0, while the other part gives

$$\pi\int_0^\infty dz\int_0^\infty dt\sin\left[z^3+\lambda(r_n-r_d)z\right]\cos\left[t^3+\lambda(r_n-r_d)t\right].$$

Appendix III—Numerical Evaluation of the Integrals

Airy[13] has tabulated values of the integral $\int_0^\infty\cos(z^3-\chi z)dz$ (in a slightly different form) over a range of values of χ from -7.57 to 7.57. This is ample for our purposes for negative values of χ. On the positive side we need to go further, but this can be done by means of Kramers' asymptotic formula,

$$\int_0^\infty\cos(z^3-\chi z)dz=\pi^{\frac{1}{2}}(3\chi)^{-\frac{1}{4}}\cos\left[2(\chi/3)^{\frac{3}{2}}-\pi/4\right].$$

The value of $\int_0^\infty\sin(z^3-\chi z)dz$ can be obtained for small values of χ in the same way that Airy obtained the values for the other integral, while for large values of χ an asymptotic value of it may be obtained by Kramers' method.[14] Since Kramers gave but a bare outline of the way his results were obtained, we shall give the calculation for the sine integral in some detail.

We make use of contours in the complex plane as indicated in Fig. 5. The lines OP and OR make angles of $\pi/3$ and $-\pi/3$, respectively, with the real axis, and the contours W_1, W_2, W_3 approach asymptotically the lines OP, OR, and OQ, the real axis, as shown. We shall indicate integrals by subscripts. Thus $\int_{OP}$ means the integral taken from 0 to ∞ along OP, $\int_{W_1}$ means the integral taken between infinite limits along W_1 in the direction shown by the arrow, etc.

Now it is readily seen that

$$2\int_0^\infty\sin(z^3-\chi z)dz=\int_0^{+i\infty}\exp(z^3+\chi z)dz+\int_0^{-i\infty}\exp(z^3+\chi z)dz.$$

By the use of Jordan's lemma we may transform the integrals from 0 to $i\infty$ and from 0 to $-i\infty$ to integrals along the lines OP and OR, respectively. Making the substitution $y=z\exp(-i\pi/3)$ or $y=z\exp(i\pi/3)$ in the result, we have

$$\int_0^{\pm i\infty}\exp(z^3+\chi z)dz=\exp(\pm i\pi/3)\times\int_0^\infty\exp\left[-y^3+\chi y\exp(\pm i\pi/3)\right]dy.$$

For small values of χ the integral on the right may be evaluated by expanding the factor $\exp(\chi y\exp(\pm i\pi 3))$ as a series in χ and integrating term by term. One gets in this way a series similar to the one used by Airy to evaluate the cosine integral. It is extremely tedious to use, however, for values of greater than 3, and for such values the asymptotic form may be used.

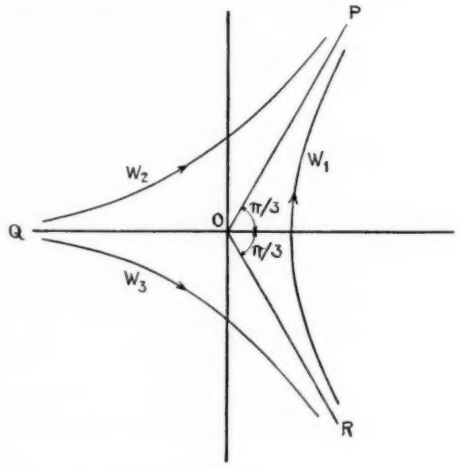

Fig. 5.

The asymptotic form will now be obtained. We note that, by Cauchy's theorem

$$\left(\int_{OP}+\int_{OR}\right)\exp(z^3+\chi z)dz = \left(\int_{W_2}+\int_{W_3}+2\int_{OQ}\right)\exp(z^3+\chi z)dz.$$

The left-hand side of this equation is, as we have noted, the quantity we wish to evaluate. It may be obtained from the integrals on the right-hand side, as follows. If χ is large $\int_{W_2}$ and $\int_{W_3}$ may be evaluated by the method of steepest descents. Setting the derivative of $z^3+\chi z$ equal to zero we see that a saddle point occurs at $z=i(\chi/3)^{\frac{1}{2}}$ for $\int_{W_2}$ and at $z=-i(\chi/3)^{\frac{1}{2}}$ for $\int_{W_3}$. Expanding by Taylor's theorem in the neighborhood of the first of these points we see that close to the saddle point we may write

$$z^3+\chi z=2i(\chi/3)^{\frac{3}{2}}+3i(\chi/3)^{\frac{1}{2}}(z-i(\chi/3)^{\frac{1}{2}})^2$$

and it is apparent that the curve of steepest descent for $\exp(z^3+\chi z)$ will have a slope of $\pi/4$. Integrating along the curve we get

$$\lim_{\chi\to\infty}\int_{W_2}\exp(z^3+\chi z)dz = \pi^{\frac{1}{2}}(3\chi)^{-\frac{1}{4}}\exp[i\{\pi/4+2(\chi/3)^{\frac{3}{2}}\}].$$

Similarly

$$\lim_{\chi\to\infty}\int_{W_3}\exp(z^3+\chi z)dz = \pi^{\frac{1}{2}}(3\chi)^{-\frac{1}{4}}\exp[-i\{\pi/4+2(\chi/3)^{\frac{3}{2}}\}].$$

Therefore

$$\lim_{\chi\to\infty}\frac{1}{2}\left(\int_{OP}+\int_{OR}\right)\exp(z^3+\chi z)dz = \lim_{\chi\to\infty}\int_0^\infty \sin(z^3-\chi z)dz = -\pi^{\frac{1}{2}}(3\chi)^{-\frac{1}{4}}\sin[2(\chi/3)^{\frac{3}{2}}-\pi/4]+\int_0^{-\infty}\exp(z^3+\chi z)dz.$$

Now to evaluate $\int_0^{-\infty}\exp(z^3+\chi z)dz$ for small values of χ we could expand $\exp \chi z$ as a series and integrate term by term, but this series will also be difficult to use for $\chi>3$. If χ is very large it is obvious that the integral approaches the value $-\int_0^\infty \exp(-\chi z)dz=-1/\chi$. This suggests that we expand $\exp z^3$ as a series and integrate term by term, but if we do this we get the asymptotic non-convergent series, $-1/\chi+3!/\chi^4-6!/2!\chi^7+9!/3!\chi^{10}-\cdots$. When $\chi=3$, the value of $1/\chi$ is 0.333 and the value obtained from the first two terms is 0.259, while the value obtained from the other expansion for the integral is 0.296. When $\chi=4$, we have $1/\chi=0.250$ and $1/\chi-3!/\chi^4=0.227$, while when $\chi=6$, we have $1/\chi=0.167$ and $1/\chi-3!/\chi^4=0.162$. At $\chi=6$, then, $-1/\chi$ will be a reasonably good value for the integral, especially as it is, for large values of χ, essentially a correction term. For values of χ between 3 and 6 we have simply made an interpolation.

TABLE III. *Values of* $\int_0^\infty \cos(z^3-\chi z)dz$ *and* $\int_0^\infty \sin(z^3-\chi z)dz$.

χ	$\int_0^\infty \cos(z^3-\chi z)dz$	$\int_0^\infty \sin(z^3-\chi z)dz$	χ	$\int_0^\infty \cos(z^3-\chi z)dz$	$\int_0^\infty \sin(z^3-\chi z)dz$
−4.0	0.020		5.7	−0.240	0.67
−3.5	0.038		6.0	0.121	0.69
−3.0	0.067	0.354	6.3	0.463	0.55
−2.5	0.112	0.408	6.6	0.720	0.28
−2.0	0.182	0.461	6.9	0.827	−0.07
−1.5	0.280	0.507	7.2	0.767	−0.43
−1.0	0.419	0.534	7.5	0.548	−0.735
−0.5	0.581	0.521	7.8	0.202	−0.908
0.0	0.773	0.446	8.1	−0.184	−0.900
0.5	0.963	0.289	8.4	−0.528	−0.708
1.0	1.110	0.039	8.7	−0.742	−0.370
1.5	1.169	−0.296	9.0	−0.765	0.030
2.0	1.078	−0.674	9.3	−0.587	0.393
2.5	0.811	−1.021	9.6	−0.250	0.619
3.0	0.384	−1.239	9.9	0.158	0.642
3.3	0.078	−1.27	10.2	0.518	0.450
3.6	−0.237	−1.21	10.5	0.724	0.094
3.9	−0.530	−1.04	10.8	0.707	−0.320
4.2	−0.756	−0.78	11.1	0.469	−0.660
4.5	−0.889	−0.47	11.4	0.080	−0.817
4.8	−0.900	−0.12	11.7	−0.337	−0.730
5.1	−0.788	0.24	12.0	−0.637	−0.426
5.4	−0.560	0.50			

The asymptotic formulas for $\int_0^\infty \sin(z^3-\chi z)dz$ and $\int_0^\infty \cos(z^3-\chi z)dz$ hold well for values of χ greater than 3. Over the range (for $\chi>3$) in which Airy has made his calculations we have calculated $\pi^{\frac{1}{2}}(3\chi)^{-\frac{1}{4}}\sin[2(\chi/3)^{\frac{3}{2}}-\pi/4]$ from his values by making use of the trigonometric relation between sine and cosine. This gives bad values when the sine is nearly zero, but one can interpolate through those points, and, in general, it seems to give better results than direct use of the asymptotic value. Outside the range of Airy's calculations the asymptotic formulas were used. I have tabulated the values of the two integrals in Table III. These values are not highly accurate, but are probably good enough for most purposes. The error may possibly be as great as 0.03 or 0.04 in the case of the sine integral for the worst part of the range where the asymptotic approximations were used; where the series or interpolation from Airy's values were used the errors in the worst cases should be under 0.01, and this is probably the upper limit of error for any part of the cosine curve.

The Deflection of Molecular Rays in an Electric Field: The Electric Moment of Hydrogen Chloride

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A comparison of the method for determining electric moments of molecules by deflection of molecular beams by inhomogeneous electric fields with the dielectric constant method shows that the molecular beam method has certain advantages. This method determines the electric moment of gases directly and is able to detect the effect of higher rotational states of non-gyroscopic molecules. Moreover, a deviation of the axis of the dipole moment from that of the axis of rotation by other than 90° should be detected. The additional energy due to an electric field is proportional to the square of the field intensity and is a function of the quantum numbers m and j, if the electric moment is perpendicular to the axis of rotation. Otherwise there will be a linear dependence on the intensity of the electric field. An experimental method of the Rabi type for studying the HCl molecule is described. The patterns produced by the undeflected and deflected molecules are given and from these patterns the electric moment of the HCl molecule is found to be approximately 1.95×10^{-18} e.s.u. *Editor.*

I. INTRODUCTION. SCOPE OF METHOD

DURING the last decade, the method of molecular rays has been notably developed as a tool in research, especially in the Institute of Physical Chemistry at Hamburg. The method aims at the production of directed, collision-free beams of neutral molecules, moving with thermal velocities in vacuo; and the study of, for example, their scattering in gases, reflection and diffraction at solid surfaces, or deflection in magnetic and electric fields. The essential feature of the method is its extreme directness; for, on the one hand, the unidirectional nature of the beams usually makes the effect of given external conditions proximately interpretable, while on the other hand their collision-free character eliminates the disturbing factor of molecular interactions. It is these features in particular which often make the method of peculiar value in the study of problems of molecular structure.

The application of the method which concerns us here is to the behavior of molecules in an electric field. An electric dipole in an inhomogeneous electric field is acted on by a ponderomotive force; hence if a ray of dipole molecules *SID*, selected by the image aperture *I* from the bundle of rays emerging from the source aperture *S*, is directed through an inhomogeneous electric field *F*, it suffers a deflection, the extent and character of which, as determined by the detector *D*, allow a determination of the molecular dipole moment, and in certain cases the deduction of details of molecular structure. (Fig. 1.)

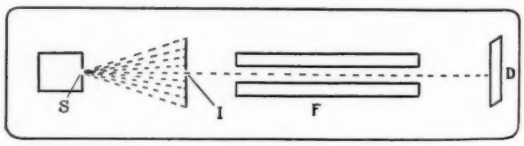

FIG. 1.

The standard method of determining molecular electric dipole moments, due to Debye,[1] depends on measurements of the dielectric constant of the substance, either as a gas, or dissolved in a non-polar solvent. The accuracy of the dielectric constant method is in most cases far in excess of that of the method of molecular rays at the present stage of its technical development. On the other hand, the deduction of the value of the dipole moment of the individual molecules from measurements of the dielectric constant of the

* The experiments described in this paper were begun by one of us (R. F.) while an 1851 Exhibitioner, in the Institute of Physical Chemistry at Hamburg (1928–29); and continued by the other (I. E.) in the Department of Chemistry of the University of California at Berkeley (1931–32), while holding a Fellowship of the Rockefeller Foundation.

[1] cf. P. Debye, *Polar Molecules*, New York, 1929.

gas or solution in bulk involves the use of often complicated statistical reasoning; which must take account, not only of the macroscopic interaction of the electric medium with the field; but also of molecular interactions, about which assumptions must be made which are often of doubtful validity, especially at high densities of the fluid. It is just in the characteristic absence of statistics from the interpretation of the results of an electric deflection experiment that the molecular rays method again shows its special heuristic advantages.

We enumerate the following more practical advantages.

(1) The dielectric constant method is subject to the limitations imposed, on the one hand by the considerable pressures required for reasonably accurate dielectric constant measurements in the gas phase, on the other by the solubility of the substance it is desired to examine in a suitable nonpolar solvent. It may therefore happen, for a given substance, not only that the temperature required to obtain the necessary gaseous pressure is inconveniently high *per se* or else leads to decomposition of the substance, but also that the substance is insoluble in nonpolar solvents. On the other hand, the pressures required in the source of a molecular beam are at the most of the order of a millimeter; and again, the applicability of the method is clearly independent of the solubility of the substance in a particular solvent. Thus the molecular rays method may prove applicable to the measurement of dipole moments in cases where the dielectric constant method fails completely; a notable example is that of pentaerythritol and its derivatives.[2]

(2) Nevertheless the discovery that symmetrically built molecules may often possess large permanent dipole moments has led one to recognize that the relative motions, of vibration or rotation, of the component parts of a complicated molecule may exert a decisive influence on its dipole moment. In certain cases, moreover, a dependence of the dipole moment on the temperature may be expected.[3] Now Debye's theory of the variation *of the dielectric constant* with temperature, which is the basis of the measurement of dipole moments by the standard method, presupposes a temperature-independent dipole moment. Thus a possible temperature variation of the dipole moment could reveal itself only as a departure of the temperature variation of the dielectric constant from that to be expected on Debye's theory. Apart from the fact that in general only a small range of temperature is available, other complications (e.g., association) impose a severe restriction on the range of the dielectric constant method, and reliable measurements of the temperature variation of the dipole moment by this method have been reported so far for isolated cases only.[4] On the other hand, since the molecular rays method measures the dipole moment *directly*, it should be immediately applicable to the study of this question, and moreover in particular to just the type of molecule which would in any case prove difficult of attack by the dielectric constant method on the grounds of (1) above. So far, no experiments of this kind have been reported.

(3) It will appear in the next section (p. 393) that if the angle between the axis of the dipole moment of a molecule and the axis of rotation is only a few degrees other than a right angle, the deflection of a beam of such molecules in an inhomogeneous electric field is very markedly greater than is the case when the axes are strictly perpendicular to one another. Thus a merely qualitative inspection of the scale of the deflection pattern might suffice to give a decision in cases where an intramolecular configuration is in doubt.

(4) It has been shown by the application of wave mechanics that in the case of non-gyroscopic diatomic molecules the contribution of the permanent dipole moment to the dielectric constant arises entirely from molecules in the lowest energy state $j=0$.[5] In such case, higher rotation states escape detection by the dielectric constant method. On the other hand, the method of molecular rays is capable of detecting, and has already detected in a qualitative way, the exist-

[2] I. Estermann, Zeits. f. physik. Chemie **B2**, 287 (1929); Estermann and Wohlwill, ibid. **20**, 195 (1933).

[3] cf. Sack, Naturwiss. **8**, 337 (1929); also Wolf and Fuchs' article *Sterischer Bau und elektrische Eigenschaften*, in Freudenberg's *Stereochemie*, Leipzig, 1932.

[4] Zahn, Phys. Rev. **40**, 291 (1932); Greene and Williams, ibid. **42**, 119 (1932).

[5] Van Vleck, Phys. Rev. **29**, 727; **30**, 31 (1927); also Debye, reference 1, p. 153.

ence of these states.[6] Further, we shall show (p. 391) that at low temperatures direct evidence of the splitting of the rotational energy levels in an electric field (quadratic Stark effect) may be expected to follow the application of the molecular rays method under the appropriate conditions. The experiments on hydrogen chloride described in the third section of this paper are a first step in this direction.

Thus the method of molecular rays offers several advantages in the study of the behavior of molecules in an electric field. Technical difficulties have hitherto made progress in this direction relatively slow; but the work which has been done, and the results which have been obtained, are sufficient to justify further development which shall make it possible to follow up some of the promising lines of advance we have indicated. We propose therefore in the remainder of this paper to outline the principles which must govern such a development and to illustrate their application to a number of problems which have already successfully been attacked, with special reference to the behavior of the HCl molecule in an electric field.

II. Theoretical

We shall restrict our discussion in the main to a simple model of a polar diatomic molecule, considered as a rigid dumb-bell; the conclusions arrived at need not therefore be immediately applicable to polyatomic molecules.

1. The time-averaged moment

If a polar molecule, moment μ, is shot into an electric field E, the *instantaneous* change of energy is of amount

$$\Delta W = \mu_E \cdot E, \tag{1}$$

where μ_E is the component of μ in the direction of E; but the molecule executes a uniform temperature rotation whose period is short compared with the time the molecule takes to traverse the field in a deflection experiment; hence μ_E changes sign every half period, the time-averaged energy change $\overline{\Delta W}$ vanishes to the first order, and the molecule is unaffected by its passage through the field.

The presence of the field, however, distorts the motion of uniform rotation of the dipole, and there results a time-averaged moment $\bar{\mu} = \beta \cdot E$, proportional to the field strength, in the direction of the field. Thus to the second order

$$\overline{\Delta W} = \tfrac{1}{2}\beta E^2. \tag{2}$$

If the center of gravity of the dipole be taken as the origin of an arbitrary system of coordinates xyz, then the components of the force acting on the dipole are clearly

$$F_x = \bar{\mu} \cdot \partial E/\partial x; \quad F_y = \bar{\mu} \cdot \partial E/\partial y; \quad F_z = \bar{\mu} \cdot \partial E/\partial z \tag{3}$$

since $\bar{\mu} = \beta \cdot E$.

According to quantum theory, $\overline{\Delta W}$ in (2) can take only certain discrete values determined by the rotational quantum number $j = 0, 1, 2, \cdots$, and the equatorial quantum number m, an integer defined by the relation $-j \leqq m \leqq j$. That is β is a function $\beta(j, m)$ of the quantum numbers j and m. The values of $\bar{\mu} = \beta(j, m) \cdot E$ for the rigid dumb-bell molecule were obtained independently by Mensing and Pauli[7] and by Kronig.[8] They are

$$\left.\begin{aligned} \bar{\mu} &= \frac{8\pi^2 I \mu^2 E}{h^2} \frac{1}{(2j-1)(2j+3)} \left(\frac{3m^2}{j(j+1)} - 1 \right) && \text{if } j \neq 0, \\ &= \tfrac{1}{3} 8\pi^2 I \mu^2 E/h^2 && \text{if } j = 0, \end{aligned}\right\} \tag{4}$$

where I is the moment of inertia of the molecule and h is Planck's constant.

For large values of j (high temperature), (4) takes the classical form

$$\bar{\mu} = \frac{\mu^2 E}{2I\omega_0^2} (3\cos^2\phi - 1) = \frac{\mu^2 E}{4\epsilon_r} (3\cos^2\phi - 1), \tag{5}$$

where ω_0 is the (unperturbed) angular velocity of rotation, ϕ is the angle between the axis of rotation and the field, and ϵ_r is the rotational energy. This expression was first obtained by Kallmann and Reiche[9]; it can be derived very simply by considerations due to Stern.[10]

[6] Wrede, Zeits. f. Physik **44**, 261 (1927); Estermann, *The Dipole Moment and Chemical Structure*, ed. P. Debye, London 1931, p. 15 ff. (Leipziger Vorträge, 1929).

[7] Mensing and Pauli, Phys. Zeits. **27**, 509 (1926).

[8] Kronig, Proc. Nat. Acad. Sci. **12**, 488 (1926).

[9] Kallmann and Reiche, Zeits. f. Physik **6**, 352 (1921).

[10] See Fraser, *Molecular Rays*, Cambridge, 1931, p. 156 ff.

The result (5) still holds for more complicated molecular types, provided that their structural symmetry is sufficient to allow their temperature motion to be referred to a single axis of rotation; and provided also that the direction of the dipole moment is normal to this axis. In a complicated molecule, however, the latter proviso may not hold; in which case it is easy to show that if the angle between the axes of dipole moment and rotation deviates by only a few degrees from normality, then in spite of temperature rotation there will remain *to the first order* a dipole moment, independent of the field strength. Hence the deflection of a beam of such molecules in an inhomogeneous electric field will be a comparatively large first order effect, not a second order effect as in the case of the dumb-bell model (cf. I(3), p. 391 above).

2. Theory of a deflection experiment

Two successful forms of the deflecting field have been devised: (a) the beam is sent parallel to a charged wire[6,11]; the directions of E and $\partial E/\partial s$ are the same (say z); $F_x=F_y=0$ in (3); (b) the beam is sent at an angle between the plates of a parallel plate condenser; E and $\partial E/\partial s$ are at right angles.[12] (See Fig. 2.)

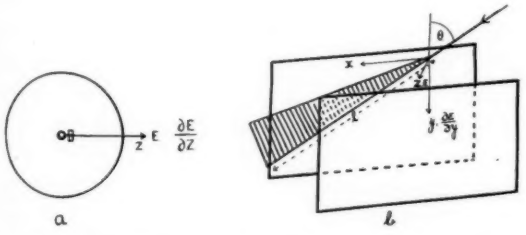

FIG. 2. Experimental arrangements for securing inhomogeneous electric fields.

In the first case, the deflection s of a single molecule at the exit of the field is given by

$$s=\tfrac{1}{4}\bar{\mu}(\partial E/\partial s)(l^2/\epsilon_v), \qquad (6)$$

where l is the length of path in the field, and ϵ_v is the energy of translation corresponding to the velocity v.

In the second case,

$$s=\tfrac{1}{4}\beta\cdot\overline{E^2}\cdot l\tan\theta/\epsilon_v \qquad (7)$$

to a first approximation; where θ is the angle of incidence of the beam, and $\overline{E^2}$ is averaged in the y direction over the distance $y'=l\cos\theta$. (See Fig. 2b.)

Eqs. (6) and (7) refer to the deflection of a single molecule, having a given velocity and value of $\bar{\mu}$ (or β). In order therefore to examine more closely the character of the deflection suffered by a beam of molecules, we must consider how the value of v and $\bar{\mu}$ permitted under the temperature conditions of the experiment by Eqs. (4) or (5) are distributed amongst the molecules of the beam. We begin with the case of high temperature.

High temperatures. Substituting the value of $\bar{\mu}$ (or β) from (5) in (6) and (7), we get

$$s=C\cdot\frac{3\cos^2\phi-1}{\epsilon_v\epsilon_r}, \quad (6a), \qquad s=C'\cdot\frac{3\cos^2\phi-1}{\epsilon_v\epsilon_r}, \quad (7a),$$

where

$$C=(\mu^2/16)\cdot E\cdot(\partial E/\partial s)\cdot l^2, \quad C'=(\mu^2/16)\cdot\overline{E^2}\cdot l\tan\theta$$

are constants of the experiment. Thus the deflection s suffered by a given molecule is decided by particular values of ϵ_v, ϵ_r, the probabilities of whose occurrence at high temperature are governed by a Maxwell distribution law; and of ϕ, all values of which are equally probable, since the beam is collision-free.

If $\epsilon_v=\epsilon_r=kT$ and $\phi=0$, the corresponding deflection is

$$s_0=2C/(kT)^2=2C'/(kT)^2, \qquad (8)$$

for the field dispositions (a) and (b) respectively; and the deflection s of any molecule referred to s_0 as norm is thus $s=\sigma\cdot s_0$.

It is convenient to calculate the intensity distribution in the deflected beam in terms of the quantity $\sigma=s/s_0$ rather than s. Fig. 3 shows the

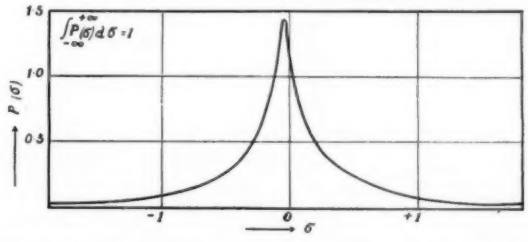

FIG. 3. Calculated intensity distribution in a deflected beam.

[11] Estermann, Zeits. f. physik. Chemie **B1**, 161 (1928).
[12] Rabi, Zeits. f. Physik **54**, 190 (1929).

result of such a calculation, assuming a parent beam of negligible width; in the figure the probability $P(\sigma)d\sigma$ for the occurrence of deflections lying between σ and $\sigma+d\sigma$, obtained by numerical and graphical integration over the individual probabilities $P(\epsilon_v)d\epsilon_v$, $P(\epsilon_r)d\epsilon_r$, $P(\phi)d\phi$, is plotted against σ.[13]

It should be noted that the molecules are still assumed to be rigid in calculating the curve of Fig. 3; actually the electron configuration is distorted by the field, resulting in a polarization $\alpha \cdot E$ of the molecule in the field direction, the deflection due to which is superimposed on the deflection arising from the time-averaged moment.

The intensity distribution in the component of the deflection pattern arising from the electron polarizability is easily shown to depend on the equations

$$\left.\begin{aligned} P_p(\sigma)d\sigma &= e^{-1/\sigma}\cdot 1/\sigma^3 \cdot d\sigma, \\ \sigma &= s/s_0, \end{aligned}\right\} \tag{9}$$

where $P_p(\sigma)d\sigma$ is the probability for the occurrence of deflections between σ and $\sigma+d\sigma$, and s_0 is obtained from (6) or (7) with α substituted for β and kT for ϵ_v. Thus an actual deflection pattern is the summation of the curve of Fig. 3 and that expressed by (9). It frequently happens, however, particularly if the field conditions are properly chosen, that the contribution of (9) to the summation curve is negligible.

The feature of the intensity distribution revealed in Fig. 3 which is of chief importance from the experimental standpoint is the fact that the maximum of the curve lies very close to the position of the undeflected beam; thus the effect observed in a deflection experiment is a diminution of intensity at the position of the undeflected trace, coupled with a broadening of the beam, rather than a lateral deviation of the beam as a whole. The way in which this diminution of intensity can be made the basis of a quantitative evaluation of the dipole moment is exemplified for HCl in Part III.

Low temperature. The deflection suffered by a molecule in a given state j, m is obtained by substituting the appropriate value of $\bar{\mu}$ (or β) from (4) in (6) or (7). In this case there is only one continuously variable quantity, namely ϵ_v; and we define $s_0(j, m)$ *for each state* j, m as the deflection of a molecule in that state having an energy of translation $\epsilon_v = kT$. Then for each state in turn we can calculate the probability $P_{j,m}(\sigma)d\sigma$ for the occurrence of deflections $\sigma_{j,m} = s(j, m)/s_0(j, m)$ lying between $\sigma_{j,m}$ and $\sigma_{j,m}+d\sigma$. Now the probability that a molecule is in the state j, m is

$$P_{j,m} = e^{-E_j/kT}/\sum_{j,m} e^{-E_j/kT}, \tag{10}$$

where E_j is the energy of rotation in the state j; the summation extends over all states, the energy differences of the states having the same j but different m being neglected. Thus the intensity distribution in a deflected beam at low temperature, containing molecules in a number of energy states, is obtained by plotting the $P_{j,m}(\sigma)d\sigma$ *vs.* σ curves for the individual states, properly weighted in accordance with (10), and constructing the summation curve. An example of such a curve, for the case of HCl at 120°K, is given in Fig. 4; for the sake of clearness, the individual $P_{j,m}(\sigma)d\sigma$ curves are shown for the three lowest rotation states only. As in the corresponding high temperature curve (Fig. 3) a parent beam of negligible width has been assumed, and the ordinates chosen to make the area under the summation curve unity. It will be seen that the lowest energy state $j=0$, which alone contributes to the observed dielectric constant, gives rise to *attracted* molecules (σ+*ve*) only in a deflection experiment. Thus the repelled molecules which have in fact been observed (at high temperature) are direct qualitative evidence of the presence of the higher rotation states (cf. I(4) above). In order to identify the individual j, m states, however, it will be necessary to carry out the deflection experiment with a velocity selector; otherwise as seen in Fig. 4, only a single maximum can be expected.

III. Experimental

1. Intensity measurements

It will have been evident, from consideration of the character of the deflection patterns of Figs. 3 and 4, that in order to evaluate the dipole moment, or in fact to make any quantitative

[13] Feyerabend, Hamburger Staatsexamensarbeit; see Fraser, reference 10, p. 162 ff.

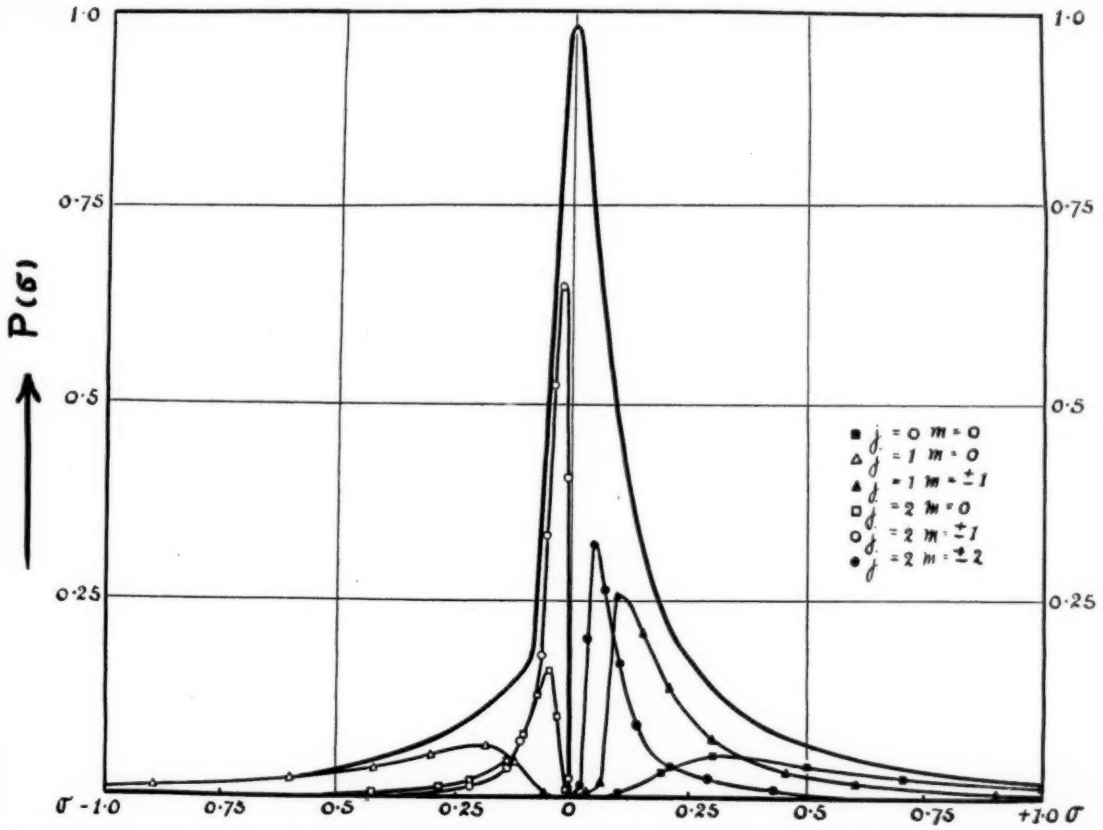

FIG. 4. Calculated intensity distribution in a beam at low temperatures taking account of the distribution of molecules in different rotational states.

deductions therefrom, a quantitative method of measuring the intensity distribution in the deflected beam was absolutely essential. The earlier work in this field had all been done using the condensation target as detector; hence the results could only be regarded at best as semi-quantitative. It was necessary to find suitable quantitative methods of detection for two chief classes of substances: on the one hand, easily condensible organic substances, where examples of the problems enumerated under I(1) and I(2) more particularly arise; on the other, gases and volatile substances which it is possible to examine at low temperature. For the first class of substances, a special form of detector making use of the heat of condensation was worked out and applied to *p*-nitranaline[14]; for the second class exemplified here by HCl, it was only necessary suitably to adapt an already existing method for the detection of gases, namely to allow the beam to enter by a slit an otherwise closed vessel containing a hot wire gauge, and to measure the resulting equilibrium pressure.[15]

2. The deflecting field

It is much easier to obtain comparatively large deflections with the charged wire field arrangement than with the parallel plate condenser. Nevertheless, the Rabi field is to be preferred for quantitative measurements on the following grounds:

(1) It is impossible except by recourse to beams of very small cross section to obtain a high inhomogeneity near a charged wire which shall at the same time be constant over the cross section of the beam.

(2) It is difficult to estimate the values of E and $\partial E/\partial s$ (Eq. (6)) near the wire on account of

[14] Wohlwill, Zeits. f. Physik **80**, 67 (1933).

[15] Knauer and Stern, Zeits. f. Physik **53**, 766 (1929).

the departure of practical arrangements from the form of the ideal cylindrical condenser; on the other hand, $\overline{E^2}$ (Eq. (7)) is readily obtained, if the plates are properly designed, from the theory of the parallel plate condenser.

(3) The field near a charged wire varies as the inverse cube of the distance from its center; hence the contribution of the electron polarization $\alpha \cdot E$ to the deflection pattern can easily become unduly prominent.

(4) The convenience of the method of estimating the dipole moment from the diminution of intensity at the position of the undeflected beam can actually make a small deviation of the maximum of the deflection pattern from that position an advantage.

For these reasons, the parallel plate condenser field was chosen for use in measuring the dipole moment of hydrogen chloride.

3. Apparatus

The apparatus in its final form is shown in Fig. 5. The beam system, consisting of the source slit *Ss*; the fore slit *Fs*; the image slit *Is*; the parallel plate condenser *C*; and the detecting system, a pair of Pirani gauges *Pg*, is mounted on a rail *R*. The upper surface of the rail is ground true, and the slits are adjusted parallel to this surface, by means of a rider carrying a knife edge, before inserting the beam system into the apparatus.

The image and fore slits are carried each on a

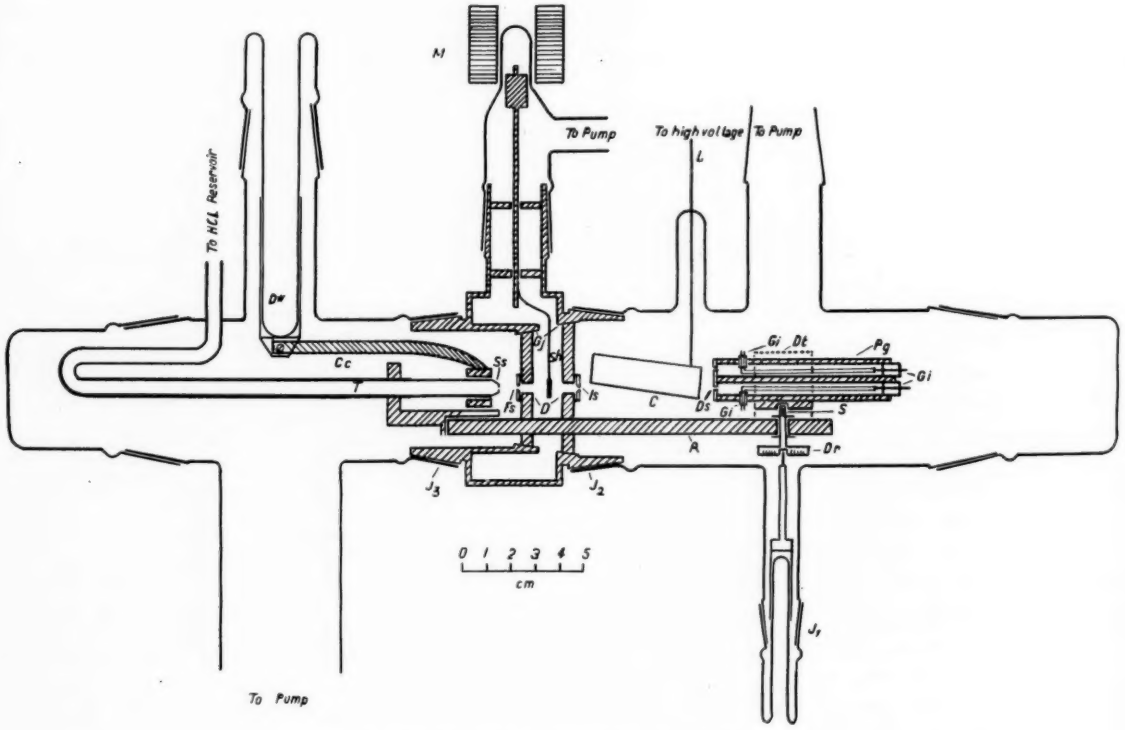

FIG. 5. Experimental arrangement of the apparatus.

very short male cone, fitting the corresponding female seating *Gj* in the central housing of the apparatus. In this way, the apparatus is divided into three chambers: the source chamber, the collimator chamber, and the observation chamber. Each chamber is separately evacuated by means of a butyl phthalate diffusion pump specially designed for high pumping speed.[16] The vacuum envelopes for source chamber and observation chamber are of Pyrex, and are connected to the central housing by the ground joints J_3 and J_2, respectively. The central hous-

[16] Estermann and Byck, Rev. Sci. Inst. **3**, 482 (1932).

ing is of Monel metal, as are all metal parts, this material having been found to resist the corrosive action of HCl rather well.

The beam is defined by the slits *Ss* and *Is*, which are 0.016 mm and 0.04 mm wide, respectively. The function of the fore slit *Fs* is not to define the beam, but to step down the vacuum from about 5.10^{-4} mm in the source chamber to about 10^{-6} mm in the observation chamber, the pressure in the central chamber being about 10^{-5} mm; its width is therefore comparatively large, about a tenth millimeter. The source slit is given a wedge-shaped form in order to reduce the Knudsen resistance between it and the fore slit, the distance between them being only 7.3 mm.

The detecting system diverges markedly in design from that used in previous work on gas beams.[15] There the detector slit was connected via a narrow tube to a glass-walled gauge outside the apparatus, the gauge being immersed in liquid air to give increased sensitivity. Now HCl is strongly adsorbed on glass walls, and moreover it is too readily condensible to make cooling profitable; therefore the gauge was made of Monel metal, and was placed inside the apparatus. In this way it was possible to make the volume of the gauge very small, thus reducing the incidence of adsorption.

The detector slit *Ds*, in the form of a canal 3 mm high, 0.04 mm wide, and 1.5 mm deep, communicates directly with the gauge; immediately above it, but outside the range of the beam, an exactly similar canal communicates with a second gauge, the function of which is the compensation of pressure and temperature variations.[15] The two gauges are made from the solid: two parallel holes are drilled in a block of Monel metal; these holes are closed at each end, at the front by plugs carrying the canals, at the rear by glass insulators *Gi* carrying each a platinum hook. Near the front end of each gauge a second glass insulator enters from the side, carrying the platinum leads for the gauge filament *F*. The latter, of platinum strip 0.05 mm wide, and 0.003 mm thick, is looped double over the platinum hook as seen in Fig. 5.

The block housing the gauges is mounted on a dovetailed slide *Dt*, and can be traversed across the beam by means of the screw *S* operated by a screwdriver carried on the ground joint J_1. The position of the detector slit *Ds* can be read off on the graduated drum *Dr*, each scale division corresponding to a movement of the detector slit of 0.01 mm.

The gauges form two adjacent arms of a Wheatstone bridge; thus stray pressure changes occurring in both gauges simultaneously are not registered by the galvanometer. A pressure change of 10^{-6} mm in the measuring gauge gave a galvanometer deflection of 3 cm at a scale distance of 130 cm; the galvanometer sensitivity was 10^{-7} volt/mm at one meter. To eliminate zero creep, timed readings were taken at intervals of 15 sec. with the beam alternately allowed to enter the detector slit and cut off therefrom by the electromagnetically operated shutter *Sh*, working in the central chamber.

The deflecting field is produced at the entrance of the parallel plate condenser *C*. One plate is mounted, with provision for adjustment, directly on the rail *R*, which is earthed via the central housing; the other plate is carried on the first by a glass *U*, and is connected by the lead *L* to a high-voltage source consisting of a transformer and one wave rectifying set (Kenotron and Leyden jar). The plates are 40 mm by 10 mm, with a gap of 2.3 mm. The angle between the edges of the plates and the beam was 7°. The edges are carefully rounded to follow in outline as far as possible the equipotentials at the entrance of an ideal parallel plate condenser; in this way it was possible to calculate the average field $\overline{E^2}$ with confidence from the theory of the parallel plate condenser.

The gas was fed to the source slit, which can be cooled if necessary by the Dewar *Dw* through a heavy flexible lead of copper *Cc*, from a reservoir in which the pressure of HCl was held constant at about 2 mm, this reservoir being fed in turn from a high-pressure reservoir through an adjustable leak. Before starting a run, however, it was found necessary to fill the apparatus with HCl at some centimeters pressure for several hours, in order first to saturate the walls of the gauges with the gas.

The intensity distribution in the beam was measured first without field, then with field, and finally again without field. Since the intensity in the parent beam is not absolutely constant, the intensity at a given point in the deflected beam

was compared with the average value of the intensity at that point observed in the bracketing runs without field; but only those complete runs in which the parent intensity remained constant to within 10 percent were accepted.

4. Results

An example of the results obtained is given in Fig. 6, which shows the intensity distribution in an undeflected beam, and that in the same beam after passage through the electric field.

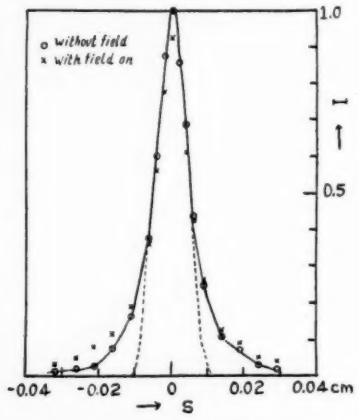

FIG. 6. Experimental distribution of molecules in a deflected and an undeflected beam.

The dipole moment of the HCl molecule is evaluated from the intensity diminution at the position of the maximum of the undeflected trace. The argument is as follows: The width of the undeflected beam is not negligible in comparison with that of the deflected beam, as was assumed in calculating the ideal curve of Figs. 3 and 4, but has the form shown in Fig. 7. Let $f(\sigma_0)$ be the equation of the curve representing it; then the equation of the deflected beam is clearly

$$F(\sigma_0) = \int f(\sigma_0+\sigma)P(\sigma)d\sigma, \qquad (11)$$

where $P(\sigma)$ is the shape of the deflected beam arising from a parent beam of negligible width, $\int P(\sigma)d\sigma$ being normalized to unity. In particular the ordinate at the center of the deflected beam, assuming it coincident with the center $\sigma_0=0$ of the undeflected beam, is

$$F(0) = \int f(\sigma)P(\sigma)d\sigma \qquad (12)$$

and is obtained by multiplying each ordinate of the undeflected beam by the appropriate $P(\sigma)$ and then integrating.

In order to evaluate μ, therefore, the abscissae of the experimental curve for the undeflected beam are reduced to the same abscissae σ as the curve of Fig. 3 for a certain assumed value of s_0 (see Fig. 7): the ordinates being reduced so that I_{max} is unity. Multiplication of each ordinate of this reduced curve by the appropriate $P(\sigma)$ gives the dotted curve of Fig. 7, the area under which (cf. Eq. (12)) represents I'_{max}, the intensity at the maximum of the deflected curve for

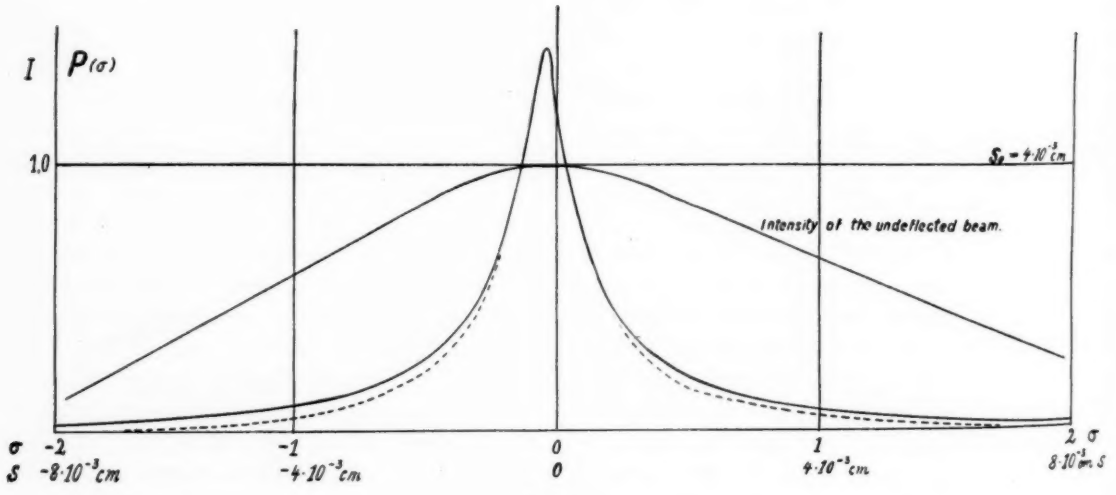

FIG. 7.

the particular value of s_0 assumed. In this way I'_{max} could be plotted as a function of $s_0=(\mu^2/8(kT)^2)\cdot\overline{E^2}\cdot l\tan\theta$ for a given set of experimental conditions.

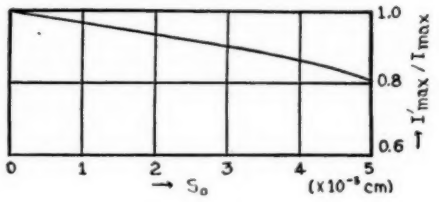

FIG. 8.

Such a plot under the conditions of the present experiments is given in Fig. 8. The value of s_0 corresponding to a given value of I'_{max}/I_{max} is read off from the curve, and μ evaluated. Table I gives a summary of the results.

TABLE I.

$\mu^2=s_0\cdot 8(k_1T)^2/\overline{E^2}\cdot l\tan\theta$

$l=4.72$ cm; $\theta=83°$; $T=290°$; $\overline{E^2}=0.6E^2$ e.s.u.; Condenser gap $d=2.3$ mm; $V=0.23E$ e.s.u.

Run No.	V kilovolt	$\frac{I'_{max}}{I_{max}}$	$10^4\cdot s_0$	$\mu\cdot 10^{18}$
I	35	0.95	14	1.69
II	32	0.97	10	1.56
III	35	0.92	24	2.21
IV	35	0.93	21	2.07
V	40	0.90	31	2.20

Mean value: $\mu=1.95\times10^{-18}\pm0.1_3$ e.s.u.*

*The limit of error given above does not of course account for systemmatic errors which may arise, e.g., in determining the form of the curve for the undeflected beam.

Two assumptions have been made in the calculations, which must be justified. (1) The maxima of the deflected and undeflected beams have been assumed coincident. Now the mean value s_0 from Table I is 2.10^{-3} cm; the value of σ at the maximum of the probability curve of Fig. 3 is 0.04; hence the displacement $\sigma\cdot s_0$ of the maximum of the deflected curve from that of the undeflected curve is $s\sim1\mu$, and can be neglected. (2) No account has been taken of the electron polarizability. The polarizability α of HCl as measured by Zahn[17] is 1.70×10^{-24} e.s.u.; with the field strengths used $\alpha\cdot E\sim2\cdot10^{-22}$; insertion of this value in Eqs. (9) shows that the effect of the polarizability on the height of the deflected maximum is less than 3 percent, and it can therefore be neglected.

Great accuracy is not claimed for the present experiments. They should rather be regarded, together with the parallel investigation on easily condensible substances referred to on p. 395, as a first attempt to obtain quantitative data on dipole moments from molecular ray experiments. It should be readily possible, for example by using narrower beams and stronger fields, greatly to improve the accuracy of the method.[18]

It is intended to repeat the experiments under improved conditions, and moreover with a cooled source slit, in order to realize the case of low temperature dealt with in Section II of this paper, where the influence of the quantum distribution of the rotational states becomes noticeable.

We are glad of this opportunity to express our several thanks to Professor O. Stern and Professor G. N. Lewis, who successively gave the above work the ready hospitality of their respective laboratories.

[17] Zahn, Phys. Rev. **24**, 400 (1924).

[18] Owing to the expiration of the Fellowship held by one of us (I. E.), the experiments had again to be interrupted; but we considered the results so far obtained to be sufficiently interesting methodically to justify publication.

Activation Energies for Reactions of Atoms in Different States

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A slight modification of Eyring's method enables the activation energy for the reaction of iodine monochloride with normal or with excited chlorine atoms to be calculated. The calculations indicate that normal chlorine atoms are much more reactive with respect to iodine chloride than are chlorine atoms excited to the $^2P_{\frac{1}{2}}$ state. Experimental evidence supporting these calculations is obtained from the results of Rollefson and Lindquist with mixtures of hydrogen, chlorine and iodine monochloride.

In the modified method, the atomic interactions—which give rise to the activation energy—are obtained from the potential energies of those molecular states which may be adiabatically formed from atoms in the particular electronic states to be considered.

A SHORT time ago Rollefson and Lindquist[1] concluded from their experiments on mixtures of hydrogen, chlorine and iodine monochloride that the reaction chains yielding hydrogen chloride were started by chlorine atoms in the $^2P_{\frac{1}{2}}$ state. Recent work,[2] especially that by Rodebush and Klingelhoefer, has shown that the reaction between chlorine atoms and hydrogen has a heat of activation sufficiently large that there should be time enough for the two lowest states of the chlorine atom to reach statistical equilibrium. Therefore, no matter what source of chlorine atoms was used, hydrogen chloride formation should be observed. Rodebush and Klingelhoefer suggest that the results (of the experiments of Rollefson and Lindquist) with iodine chloride are due to chlorine atoms reacting more readily with some other substance than hydrogen. The truth of this is apparent since iodine chloride is a powerful inhibitor for hydrogen chloride formation. It has been suggested[1] that this may be caused by a reaction such as $ICl+Cl=Cl_2+I$. To account for the observed phenomena fulfillment of a second condition is necessary: normal chlorine atoms must be removed more readily than excited ones. This second requirement is readily fulfilled by postulating that $ICl+Cl=Cl_2+I$ is very much faster than $ICl+Cl^*=Cl_2+I$. This may seem to be very improbable since it requires an excited atom to be less reactive than the corresponding unexcited atom. We shall show that considerations based on thermodynamics and the quantum theory of activation lead to just this conclusion.

The use of quantum mechanics in the calculation of activation energies has been presented in great detail in papers by Eyring and Polanyi[3, 4]; the second reference deals especially with the reactions of the halogen atoms. However, in Eyring's calculations, no distinction is made between the reactions of halogen atoms in the $^2P_{\frac{1}{2}}$ state and those in the $^2P_{\frac{3}{2}}$ state. The calculations are all made for the halogen atoms in the $^2P_{\frac{3}{2}}$ state.

The approximate values of the interaction terms in the equation

potential energy

$$=Q+\tfrac{1}{2}(2)^{\frac{1}{2}}[(\alpha-\beta)^2+(\beta-\gamma)^2+(\gamma-\alpha)^2]^{\frac{1}{2}}$$

are usually obtained from the potential energy functions for the corresponding diatomic molecules. Now if we consider the reaction $ICl+Cl^*=I+ClCl^*$, the interaction terms are to be derived from the energies of the molecules ICl, $ClCl^*$, and ICl^*. If Cl^* is in the $^2P_{\frac{1}{2}}$ state and the other two atoms are in the $^2P_{\frac{3}{2}}$ state, then we must obtain our interaction terms from ICl ($^1\Sigma$),

[1] Rollefson and Lindquist, J. Am. Chem. Soc. **52**, 2793 (1930); **53**, 1184 (1931).

[2] Rodebush and Klingelhoefer, J. Am. Chem. Soc. **55**, 130 (1933); H. v. Hartel, Zeits. f. physik. Chemie **B11**, 96 (1930).

[3] Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).

[4] Eyring, J. Am. Chem. Soc. **53**, 2537 (1931).

Cl_2 ($^3\Pi_0$), and ICl ($^3\Pi_0$).[5, 6] The reasons for this choice of states are: (1) ICl ($^1\Sigma$), case under consideration. (2) Cl_2 ($^3\Pi_0$), a $^2P_{\frac{3}{2}}$Cl atom and a $^2P_{\frac{1}{2}}$Cl atom cannot form a normal molecule. (3) ICl ($^3\Pi_0$), a $^2P_{\frac{3}{2}}$I atom and a $^2P_{\frac{1}{2}}$Cl atom cannot form a normal molecule. This treatment permits us to differentiate between the reaction of an ICl molecule with a chlorine atom in the $^2P_{\frac{1}{2}}$ state and one in the $^2P_{\frac{3}{2}}$ state, for in the latter case all the interactions would be obtained from the $^1\Sigma$ terms.

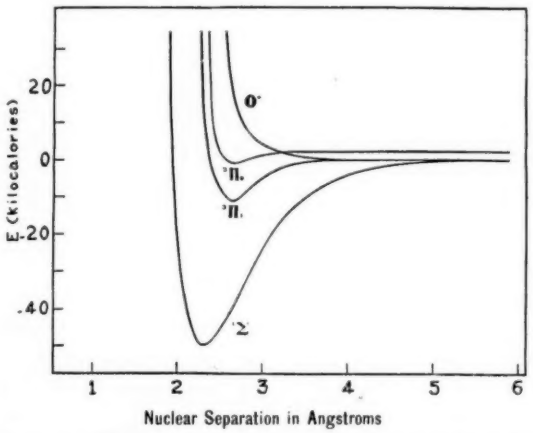

FIG. 1. Potential energy diagram for ICl. The states marked $^1\Sigma$, $^3\Pi_1$, and O^+ are formed by an iodine atom in the $^2P_{\frac{3}{2}}$ state and a chlorine atom in the $^2P_{\frac{3}{2}}$ state; the $^3\Pi_0$ state is formed by a normal iodine atom ($^2P_{\frac{3}{2}}$) and an excited $^2(P_{\frac{1}{2}})$ chlorine atom. The diagram for the chlorine molecule is similar[8] except that transitions involving the $^3\Pi_1$ and O^+ states have never been observed experimentally.

In order to explain the experimental results of Rollefson and Lindquist it is not necessary to make the activation energy calculations for both of the reactions,

$$I^2P_{\frac{3}{2}}Cl^2P_{\frac{3}{2}}+Cl^2P_{\frac{3}{2}}=I^2P_{\frac{3}{2}}+Cl^2P_{\frac{3}{2}}Cl^2P_{\frac{3}{2}}. \quad (1)$$

$$I^2P_{\frac{3}{2}}Cl^2P_{\frac{3}{2}}+Cl^2P_{\frac{1}{2}}=I^2P_{\frac{3}{2}}+Cl^2P_{\frac{3}{2}}Cl^2P_{\frac{1}{2}}. \quad (2)$$

Reaction (1) is exothermic by an amount equal to the difference between the heats of formation of ICl and Cl_2 (from normal atoms), approximately 7 kilocalories. We calculate the corresponding heat of activation to be about 4 kilocalories. To calculate the heat of reaction (2) we use the heat of formation of iodine chloride (from normal atoms) and the heat of formation of the $^3\Pi_0$ state of Cl_2. This latter[7] is only 9.6 kilocalories which makes reaction (2) endothermic to the extent of 40 kilocalories. According to the first law of thermodynamics it would be necessary to supply at least this much energy if the reaction is to proceed. Hence this is a minimum value for the heat of activation and without further calculation we may say that reaction (2) is very slow compared with reaction (1). Expressed in other words, by activating the chlorine atom to the $^2P_{\frac{1}{2}}$ state we have rendered it much less reactive toward ICl. This does not mean that if we introduce a large number of $^2P_{\frac{1}{2}}$ chlorine atoms into some iodine chloride vapor that no reaction would occur; we must remember that collisions would eventually transfer the chlorine atoms to the $^2P_{\frac{3}{2}}$ state and then the reaction would proceed according to (1). From the experimental results of Rollefson and Lindquist we conclude that such energy transfers have a probability sufficiently low so that many of the excited atoms survive long enough to react with hydrogen.

At the present time the possibility of extending these considerations to other reactions is limited by insufficient knowledge of the higher electronic states of most molecules. It may be that in those cases where there is a marked discrepancy between the experimental activation energies and those calculated by Eyring that the discrepancy would be greatly reduced if the calculation, in which the higher states are considered, could be made.

[5] See Fig. 1.

[6] Providing no electronic change takes place as the atoms approach.

[7] Weitzel, Handbuch der Experimental Physik, Erganzungswerk I, 383–385 (1931). Akademische Verlagsgesellschaft, Leipzig.

[8] Mullikan, Phys. Rev. 36, 669, 1440 (1930); Rev. Mod. Phys. 4, 17, 70 (1930).

The Vibration Spectra and Structure of the Cyanogen Halides

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The Raman spectra of the cyanogen halides in the liquid state or in alcoholic solution contain 3 frequencies ν_1, ν_2, and ν_3. In the order chloride, bromide, iodide, $\nu_1 = 2201$, 2187, 2158 cm^{-1}; $\nu_2 = 729$, 580, 470; $\nu_3 = 397$, 368, 321; the order of intensities of Raman transitions is $\nu_1 > \nu_2 > \nu_3$. The relative values of the frequencies indicate a linear arrangement of the nuclei in the lowest electronic state of these molecules, and the data are in accord with the structure X−C≡N rather than X−N=C.

THE following report contains the results of experiments designed to establish the fundamental vibration frequencies of the unsymmetrical triatomic molecules, the cyanogen halides, by investigating the Raman spectra of these compounds, and the evidence on the debated matter of their structure afforded by a knowledge of these frequencies.

Experimental

Cyanogen chloride was easily obtained in a pure condition by passing chlorine into the double cyanide of zinc and potassium according to Mauguin and Simon's modification of Held's method.[1] The bromide was a commercial product, while the iodide was prepared by the action of mercuric cyanide on iodine in ether solution.[2] The chloride and bromide were examined in the liquid state. The chloride, whose boiling point is 15°C, was condensed in a well cooled scattering tube, which was sealed off when filled. The spectrum was examined at room temperature (18°C). The bromide, which melts at 52° and boils at 61°, was examined in a tightly stoppered tube 2 inches long, placed in a bath of acetone vapor (B.P. 56°).

The iodide melts only under pressure. There is, however, sufficient decomposition of the substance at the melting point, about 146°, to color the liquid dark red, and it was impossible to obtain the spectrum of the pure liquid. The substance was investigated dissolved in methyl alcohol, in which it is very soluble in the cold without undergoing chemical change.

[1] Mauguin and Simon, Ann. Chim. **15**, 18 (1921).

[2] Linnemann, Annalen **120**, 36 (1862).

The source of light was a Hanovia 220 volt quartz mercury arc, focussed by a large glass condensing lens on the scattering tube, and the spectrograph was a Hilger constant deviation instrument with a dispersion of about 100 cm^{-1} per mm in the blue and violet. Spectra were photographed both with the lines of wave-length 4047A and the group about 4358A as exciting lines and with the former line removed by means of a filter composed of two plates of Noviol O glass. A solution of *p*-nitro toluene in alcohol is also very suitable for removing 4047 without appreciably dimming 4358, and was used in the later experiments. The substances gave relatively strong Raman spectra with comparatively little background.

Table I.

ClCN			BrCN			ICN		
ν cm^{-1}	Source	$\Delta\nu$ cm^{-1}	ν cm^{-1}	Source	$\Delta\nu$ cm^{-1}	ν cm^{-1}	Source	$\Delta\nu$ cm^{-1}
22541	e	397	22572	e	368	22617	e	321
22501	a	2202	22516	a	2187	22549	a	2156
22321	b	2195	22360	e	580	22468	e	470
22263	d	732	20754	e	2186	20780	e	2158
22219	e	729						
22129	e	809						
20848	c	2191						
20786	d	2201						
20736	e	2200						

The results are summarized in Tables I and II, and microphotometer curves are reproduced in Fig. 1. The column headed source refers to the line in the Hg spectrum causing the Raman line. The wave-lengths of Hg lines concerned are a, 4047; b, 4078; c, 4339; d, 4348; e, 4358a. The figures in parenthesis after the vibration frequencies in Table II give a rough estimate of the relative intensities of the Raman transitions. The

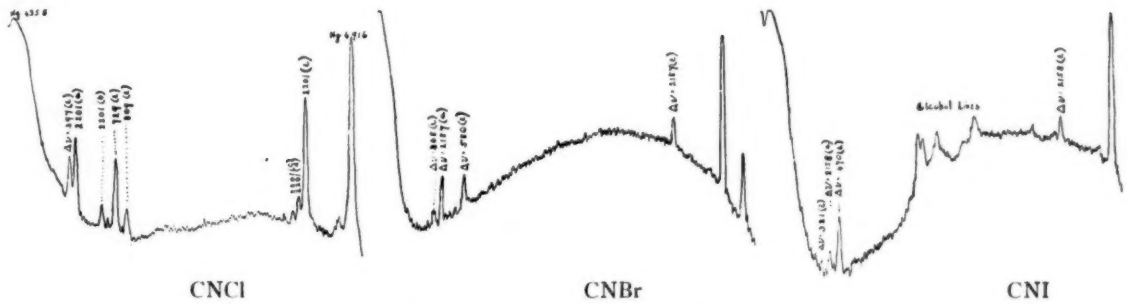


FIG. 1. Raman spectra of cyanogen halides.

feeble Raman line in the spectrum of ClCN of $\Delta\nu$ 809 cm^{-1} seems most probably to originate in a transition involving the oscillation of fundamental frequency 397 in which the vibrational quantum number increases by 2.

TABLE II. *Fundamental vibration frequencies of cyanogen halides.*

	ν_1 cm^{-1}	ν_2 cm^{-1}	ν_3 cm^{-1}
ClCN	2201 (10)	729 (5)	397 (3)
BCN	2187 (10)	580 (5)	368 (2)
ICN	2158 (10)	470 (2)	321 (1)

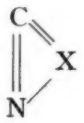
DISCUSSION

Although the cyanogen halides have been known for over a century, there is still uncertainty as to their constitution, the choice being, in the symbolism of organic chemistry between the structures

$$\underset{(1)}{X-C\equiv N} \quad \text{and} \quad \underset{(2)}{X-N=C=} \quad \text{or} \quad \underset{(3)}{X-N\equiv C.}$$

Nitrile — Carbylamine

Gutman[3] has also proposed a cylic formula



which, however, with trivalent halogen, seems inherently improbable and is excluded by the results we have obtained.

The weight of opinion on the side of organic chemists seems to incline to the carbylamine formula (2),[4] modified by arguments that the chloride is a carbylamine, the iodide a nitrile, and the bromide a tautomeric mixture of the two.[5] The cyanogen halides in fact show the chemical behavior neither of typical compounds containing a well-defined nitrile group nor yet of those containing a nitrogen-halogen linkage—they are much more stable than any compound which we have been able to find reference to as definitely containing a nitrogen halogen linkage. Nor, it must be admitted at the outset, do the results we have obtained on the fundamental vibrations of the compounds, permit a completely definitive answer to be made as to their linkages, though there is no suggestion that the linkages are not of the same nature in all three compounds.

In the first place it is to be noted that the comprehensive work of Dadieu and Kahlrausch on organic C−N compounds shows that the great differences in chemical behavior which exist between authentic nitriles and authentic carbylamines is not well expressed by the distinction between a triple and a double bond between C and N as indicated in formulae (1) and (2).[6] The Raman spectra of the alkyl nitriles show a remarkably constant frequency of 2245 cm^{-1} which is undoubtedly due to the vibration between the C and N atom, and which is about the magnitude to be expected for the vibration of the triple bonded group C≡N. The alkyl carbylamines have a different, but not markedly different frequency at 2180 cm^{-1}; and it is impossible to ascribe such a small change in vibration frequency to a change in linkage represented

[3] Gutman, Ber. **42**, 3623 (1909).

[4] Chattaway and Wadmore, J. Chem. Soc. **81**, 192 (1902).

[5] C. V. Zappi, Bull. Soc. Chim. **47**, 453, 537 (1930); **49**, 397 (1931).

[6] Kahlrausch, *Der Smekal-Raman-Effekt*, p. 319 et seq. (Julius Springer, Berlin, 1931).

by the difference between a triple and a double bond; the bond C=N would in fact have a frequency near 1700 cm^{-1}. It is possible to write electronic formulae for the two classes of compounds which are completely analagous.

$$\underset{\text{carbylamine}}{H:N\vdots C:} \quad \text{and} \quad \underset{\text{nitrile}}{H:C\vdots N:}$$

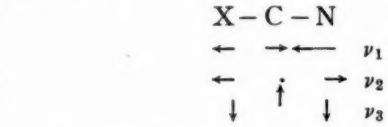
and these are probably a better representation of the state of binding in the unexcited state of the 2 molecules than the conventional bond formulae.

Returning to the evidence provided by a knowledge of the vibration frequencies of the cyanogen halides on the alternative structures, one finds that, if not absolutely conclusive, it is strongly in favor of the nitrile constitution for all three compounds. The carbon-nitrogen frequency in the chloride, 2201 cm^{-1}, is decidedly higher than the value for the aliphatic carbylamines, 2180 cm^{-1}. True, it is lower than the value 2245 cm^{-1}, characteristic of the aliphatic nitriles, but it is likely enough, and in accord with experience in similar cases, that substitution of a heavy Cl atom for the one or two C atoms in the alkyl group which alone influence the C−N vibration should lower the value of this frequency, as is shown by its progressive diminution in the bromide and iodide. The observed value of the frequency for CN I is only 12 cm^{-1} lower than that for methyl carbylamine whereas substitution of a heavy iodine atom for the CH_3 group would have been expected to diminish it much more considerably, probably by about 80 or 90 cm^{-1}. In the conclusion that all three halides have the same structure we are in agreement with that of Badger and Sho-Chow Woo[7] who, as a result of their study of the continuous ultraviolet absorption spectra of these compounds, advance cogent reasons based on a discussion of binding energies for preferring the nitrile structure.

Shape of the Molecule

It may first be relevent to refer to the conclusive proof given by Barker and Kya Nam Choi[8] in their rotational analysis of the infrared absorption bands of HCN that this molecule is linear.

In the following discussion we shall assume that the linkage is X−C−N where X is the halogen. A triatomic molecule will have $3\times3-6=3$ degrees of vibrational freedom if bent and $3\times3-5=4$ degrees if linear. In the latter case, two of the frequencies, those corresponding to the bending of the molecule in two perpendicular planes, are equal if the binding forces are axially symmetrical. Three fundamental frequencies will therefore exist, all of which appear in the Raman spectra in the case of the cyanogen halides. Anticipating the result that the frequencies observed for these compounds are in accord with a linear molecule, we may represent the vibrations as follows:



The solution of the mechanical problem of the motion of 3 point masses under the action of "valence" forces has been given by Lechner[9] who finds the condition that for a linear arrangement of the masses, m_1, m_2 and m_3.

$$\frac{\nu_1}{\nu_2}+\frac{\nu_2}{\nu_1}>2k, \text{ where } k=1-\frac{\mu_{12}\mu_{23}}{m_2^2},$$

$$\mu_{12}=\frac{m_1m_2}{m_1+m_2}, \quad \mu_{23}=\frac{m_2m_3}{m_2+m_3}.$$

The values for $\nu_1/\nu_2+\nu_2/\nu_1$ and $2k$, respectively, are: chloride, 3.36, 2.60; bromide 4.00, 2.74; iodide 4.84, 2.80. The observed frequencies are compatible with a linear arrangement of the atoms.

It is of some interest to calculate the force constants, the restoring force for 1 cm displacement of the atoms in the various vibrations when the latter remain simple harmonic. According to Lechner, these are given for the unsymmetrical linear three-point-mass model by

$$n_1^2+n_2^2=f_{12}/\mu_{12}+f_{23}/\mu_{23},$$

[7] Badger and Woo, J. Am. Chem. Soc. **53**, 2542 (1931).

[8] Barker and Choi, Phys. Rev. **42**, 777 (1932).

[9] Lechner, Sitz. Wien. Akad. Math.-natur. Classe **141**, 2a, 291 (1932).

$$n_1^2 n_2^2 = \frac{f_{12}}{\mu_{12}} \cdot \frac{f_{23}}{\mu_{23}} \left\{ 1 - \frac{\mu_{12}\mu_{23}}{m_2^2} \right\},$$

$$n_3^2 = d/\mu_4.$$

If ν is the frequency of vibration in cm^{-1} and m is given in atomic weight units (Cl = 35.46, etc.), n^2 is defined as equal to $4\pi^2c^2\nu^2/N = 5.863 \times 10^{-2}\nu^2$, where N is Avogadro's number. f, the restoring force for stretching displacements and d, the restoring force for the bending displacement are then given in dynes per cm.[10]

d and μ_4 are defined by the relation

$$\frac{1}{\mu_4} = \frac{1}{\mu_{12}} \frac{s^2}{s_{12}^2} + \frac{2}{m_2} \frac{s^2}{s_{12}s_{23}} + \frac{1}{\mu_{23}} \frac{s^2}{s_{23}^2}$$

where S_{12}, S_{23} are the distances between m_1 and m_2 and m_2 and m_3, respectively, and $d_{12}s_{12}^2 = d_{23}s_{23}^2 = ds^2$. d_{12} is the restoring force for a bending displacement of m_1, m_3 being fixed and similarly for d_{23}.

The values of the force constants are given in Table III. The calculation of the bending forces

TABLE III.

	f_{12}	f_{23}	d (approx.)
ClCN	5.14×10^5 dynes/cm	16.65×10^5 dynes/cm	0.17×10^5 dynes/cm
BrCN	4.16	16.84	0.15
ICN	2.60	16.80	0.11

requires a knowledge of the interatomic distances which are unknown in these compounds. If as a first crude approximation the distances S_{12} and S_{23} are assumed equal, $s_{12} = s_{23} = s$, and $1/\mu_4 = 1/\mu_{12} + 2/m_2 + 1/\mu_{23}$, whence the above values of d are obtained.

Comparison of the frequencies ν_1 and ν_2 in the cyanogen halides with those exhibited by other compounds containing the C≡N and C⁻ halogen linkages shows that these molecules are further illustrative of the preservation of "bond frequencies" in polyatomic molecules. The frequency ν_1 has approximately the same value, about 2200 cm^{-1} in all three of the halides, and all compounds containing the linkage C≡N, including the diatomic CN molecule known from spectroscopy, have a frequency not very different from this value. In the same way, the frequency $\nu_2 = 729$ for cyanogen chloride is close to the strong frequency 710 in CH_3Cl; ν_2 for the bromide is nearly the same as the frequency 594 in CH_3Br, and the value 469 for the iodide is comparable with the frequency 522 in CH_3I. It would therefore be possible to make the statement that the vibration spectra of the cyanogen halides are partially composed of C≡N and C⁻ halogen bond frequencies, and to identify these frequencies with ν_1 and ν_2, respectively. Although the calculation of the force constants is in terms of a dynamical model in which the frequencies ν_1 and ν_2 involve all of the masses, in consequence of which it becomes impossible to attach meaning to C≡N and C⁻ halogen vibrations, the experimental fact of the persistence of "bond vibrations" in polyatomic molecules nevertheless suggests the reasonableness of identifying the constant f_{23} as the "force constant for the C≡N vibration" and the constant f_{12} with the "force constant for the C-halogen vibration." In fact, the constant f_{23} is very close to the constant which is obtained from the experimental value of the frequency in the normal state of the diatomic CN molecule, 2069 cm^{-1}, on the assumption of a simple harmonic oscillation, namely 16.3×10^{-5} dynes/cm. The very small variation of f_{23} in the three halides leads to the conclusion that the carbon-nitrogen linkage is the same in all three compounds, while the steady diminution of f_{12} with increasing atomic weight of the halogen indicates a weakening in this linkage which is in accord with the chemical behavior of the compounds.

Our thanks are due to Mr. Edward Shriver of this department who very kindly obtained the microphotometer curves.

[10] Kohlrausch, *Der Smekal-Raman-Effekt*, pp. 154, 170.

The Raman Spectra of Ring Compounds. I. Mono-Substituted Benzene Compounds

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An improved apparatus for the study of Raman spectra has been developed. The use of filters including nitrobenzene for removing violet light, sodium nitrite for removing ultraviolet and copper nitrate for the removal of red light, has been discussed. The Raman spectra of *n*-butane, chlorobenzene, bromobenzene and iodobenzene have been reinvestigated and several new lines found in each. The Raman spectrum of alpha-chloropyridine has been studied for the first time and found very similar to that of chlorobenzene.

THE problem of the structure of the benzene ring has long been of interest to chemists and has attracted the attention of many investigators in the field of Raman spectra. In the five years since the opening of this field, at least thirty-five papers dealing with the Raman spectrum of benzene have appeared, and although the most careful and painstaking work has been done on this compound, authentic new lines are still being reported. In view of this fact and the importance of the problem of the structure of the benzene ring, it has seemed worth while to apply the best current technique to a repetition of the earlier work on the simpler aromatic derivatives. There seems to be a reasonable hope of obtaining, with the present methods, a series of spectra complete enough for the solving of the major points in the analysis of the modes of internal vibration of these molecules.

With these facts in mind, we have photographed the Raman spectra of a group of aromatic compounds and present, in this and a subsequent article, the results obtained. In addition to the data themselves, there are certain improvements in technique which may also be of interest; especially those designed to facilitate the study of compounds of high melting point and unusual fluorescence.

I. APPARATUS

In connection with this work, an illuminating apparatus of great power has been constructed. (Figs. 1 and 2.) The illuminator is built around a Pyrex tube *A* of 48 mm inside diameter. The annular space between this tube and the Raman tube *B*, which is mounted at its axis, may be used for filters and for heating or cooling when necessary. The light is furnished by four quartz capillary mercury arcs *G*, of the type described by Langer and Meggers,[1] operating in running water. The water jacket can *C*, which also serves as a reflector, is of chromium plated brass and has the form of a combination of four ellipses as in the apparatus described by Anand.[2] This can is supported and held in shape by a set of horizontal plates *D* whose centers are cut out to fit

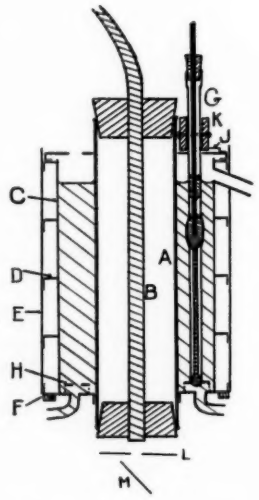

FIG. 1. Raman apparatus.

* From the dissertation submitted by John W. Murray to the Board of University Studies of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] Langer and Meggers, Bur. Standards J. Research **4**, 711 (1930).

[2] B. Anand, J. Sci. Inst. **8**, 258 (1931); **9**, 324 (1932).

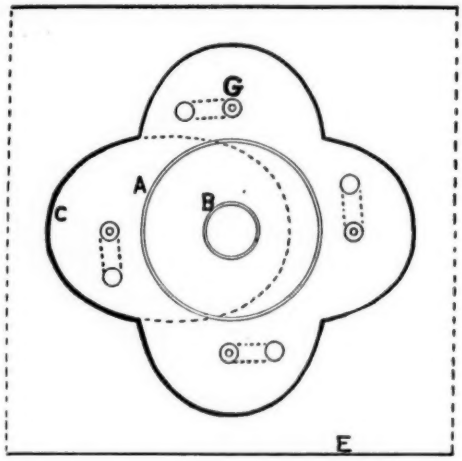

FIG. 2. Diagram of reflectors.

it and these in turn are bolted to two vertical plates E and the whole is mounted on a ring by means of the rods F. The arcs are aligned at the outer foci of the ellipses by adjustment of the racks H and J which hold the bases of the arcs and the transite handles K in position. A large fraction of the light is thus reflected into the Raman tube which lies at the common focus of the set of ellipses. Scattered light passes downward through the window and the stop L and is reflected by the mirror M to the spectrograph which is placed at a distance of about 8 feet in order to eliminate reflected light from the walls of the tube. The spectrograph used in this work is a Bausch and Lomb glass prism instrument with F 10 lenses and has a dispersion of 17A per mm at 4000A and 50 at 5000A.

For liquids, a tube of the Wood type may be used as shown in Fig. 1. Two types of tubes have been designed for the study of high-melting compounds which must be distilled continuously during the run on account of decomposition. (Fig. 3, I and II.) The first type is simpler but bulkier. The whole tube is of Pyrex glass and is heated with a winding of nichrome wire. The bulb N is heated by a separate circuit at a higher temperature so that distillation takes place from N to O. The bend below O is sooted to furnish a black background. In the second type, the two tubes are concentric and the depressed part serves as a condenser while the horn Q is sooted to give the black background. The distillate falls into the funnel at the top of the inner tube. When

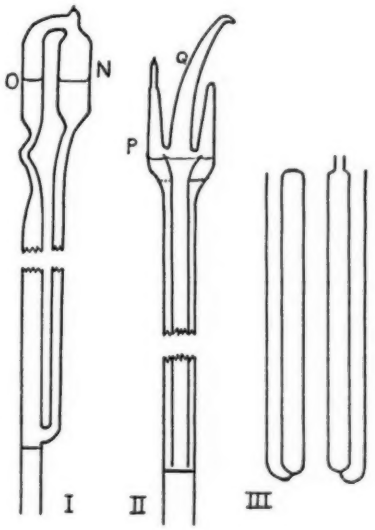

FIG. 3. Raman tubes for continuous distillation (I and II) and cell for use with three liquid filters (III).

distillation is not required, the tube used is like type I with the distilling arm omitted. In either case, the tube is mounted inside of a straight jacket tube which replaces the Raman tube B in Fig. 1. The jacket may be lined with mica for thermal insulation.

The filters are arranged in annular layers in the space between A and B, as in the apparatus described by Dadieu and Kohlrausch.[3] The cell shown in Fig. 3, III, permits the use of three layers of liquid filters, two in the cell and one outside. The cell may be simplified in an obvious manner when only two layers are needed. Glass filters may be used with this apparatus either as tubes or as sets of four plates.

The use of filters is practically necessary for the location of the weaker lines of the spectrum. Three distinct purposes are served: simplification of the spectrum, removal of continuous background from the mercury arc, and protection against decomposition and fluorescence from short wave radiation. For excitation with the blue mercury lines, a one mm layer of nitrobenzene will completely suppress the violet lines while transmitting most of the blue. It darkens with use but compares favorably, in this respect,

[3] See Kohlrausch, *Der Smekal-Raman-Effekt*, Springer, Berlin (1931).

with quinine sulfate which is in general use for this purpose. A 2 mm layer of a saturated sodium nitrite solution will protect the nitrobenzene against ultraviolet light so that its transmission of the blue light is but slightly reduced by an eight hour exposure. Pfund[4] has recently recommended the use of sodium nitrite solution for the purpose for which nitrobenzene is used here. It has the advantage of stability but its relative transmission of blue to violet light is far inferior to that of nitrobenzene. It is, however, very useful for the purpose described above and also, in lesser concentrations, for removing ultraviolet when exciting with the violet lines. An excellent combination for excitation with the blue lines is: 2 mm of saturated sodium nitrite solution, 1 mm of nitrobenzene, and 10 mm of saturated praseodymium nitrate solution to remove the continuous background. The nitrobenzene may be diluted with alcohol and crystal violet may be added to remove the blue-green region. For excitation with the violet lines, a 2 mm layer of Corning Red Purple Ultra glass is useful for removing the blue. This compares favorably with iodine in carbon tetrachloride which is often used for this purpose. A layer of sodium nitrite is used with one of these filters and is more efficient than Noviol glass. When excitation with the green line is necessary, as with some colored or fluorescent substances, a combination of potassium chromate, copper nitrate, and neodymium (or didymium) nitrate gives almost complete isolation of the 5461 mercury line. Excitation by this line is sometimes of value in deciding questions as to the origin of lines of low displacement.

The apparatus described above will record the strong Raman lines of benzene in thirty seconds. Exposures of several hours with strong filters are generally used in order to obtain the weaker lines.

II. Results

The Raman spectrum of *n*-butane was investigated for the purpose of obtaining data for thermal calculations. Since this work was done, results of an earlier investigation by Bhagavantam[5] have appeared which are in good agreement with those reported here. The material used was 99 percent commercial *n*-butane and was distilled twice before using. Chlorobenzene, bromobenzene and iodobenzene have been reexamined and a number of new lines have been found. These compounds have been studied by

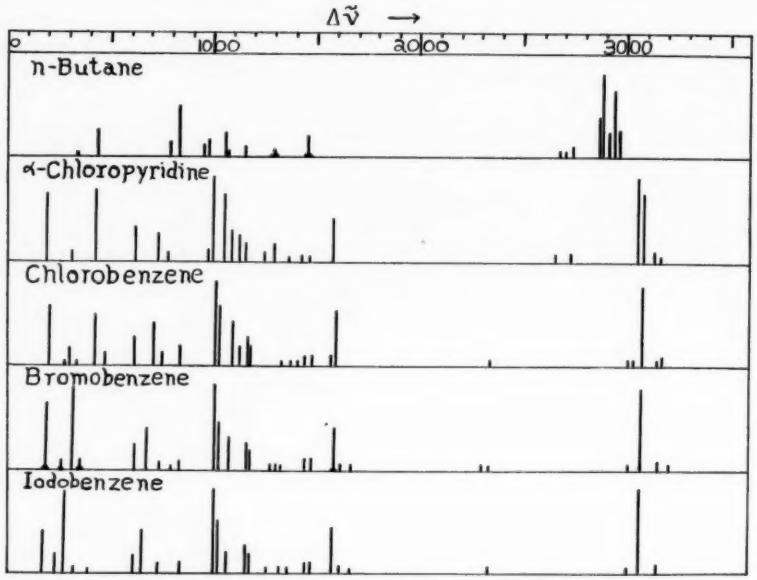

FIG. 4. Raman displacements of compounds studied.

[4] A. H. Pfund, Phys. Rev. **42**, 581 (1932).

[5] S. Bhagavantam, Ind. J. Phys. **6**, 595 (1931).

several earlier workers.[6] The material used was specially purified for specific heat studies by Mr. D. E. Teets of this laboratory. Alpha-chloropyridine has been studied for the first time. This substance was prepared by Dr. Lyman C. Craig of this laboratory. The results obtained are recorded in the following tables and are presented graphically in Fig. 4.

The procedure advocated by R. W. Wood,[7] of taking two plates of each substance using different exciting lines, has been employed. The violet and blue mercury lines have been used in all cases and the green line in some. In the cases in which it has not been necessary to remove the ultraviolet to prevent decomposition, Raman lines excited by the 3650 group appear with the lines from the violet. This is very evident in the photograph of *n*-butane shown in Fig. 5. The use of several exciting lines makes it possible to decide questions arising from excitation by the

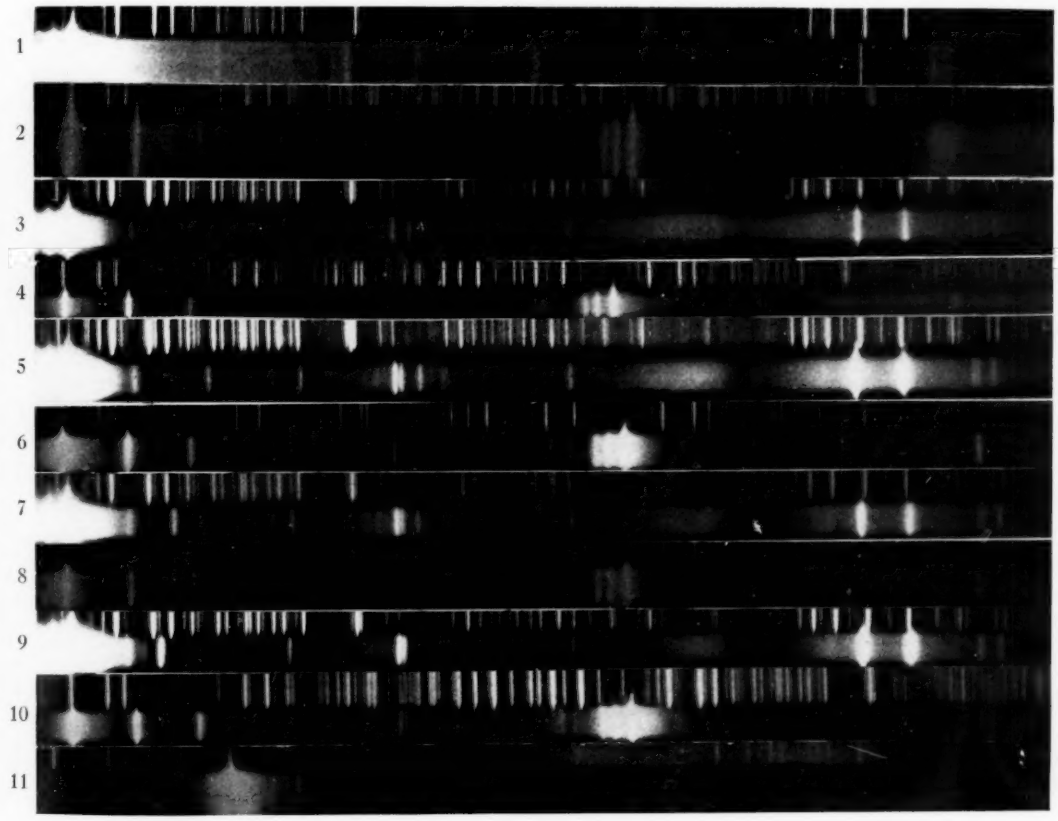

FIG. 5. Raman spectra.

1. *n*-Butane excited by $\lambda=4358$
2. *n*-Butane excited by $\lambda=4047$
3. α-Chloropyridine excited by $\lambda=4358$
4. α-Chloropyridine excited by $\lambda=4047$
5. Chlorobenzene excited by $\lambda=4358$
6. Chlorobenzene excited by $\lambda=4047$
7. Bromobenzene excited by $\lambda=4358$
8. Bromobenzene excited by $\lambda=4047$
9. Iodobenzene excited by $\lambda=4358$
10. Iodobenzene excited by $\lambda=4047$
11. Iodobenzene excited by $\lambda=5461$

[6] Pringsheim and Rosen, Zeits. f. Physik **50**, 741 (1928); Petrikaln and Hochberg, Zeits. f. physik. Chemie **B3**, 217, 405 (1929); Dadieu and Kohlrausch, Monats. f. Chem. **52**, 379 (1929); **57**, 488 (1931); Dadieu, Kohlrausch and Pongratz; Monats. f. Chem. **61**, 426 (1932); Langseth, Nature **124**, 92 (1929); Fujioka, Sci. Pap. Inst. Phys. Chem. Res. Tokyo **11**, 205 (1929); Cleeton and Dufford, Phys. Rev. **37**, 362 (1931); Bhagavantam and Venkateswaran, Proc. Roy. Soc. (London) **A127**, 360 (1930); Wood, Phys. Rev. **38**, 2168 (1931).

[7] Wood, Phys. Rev. **38**, 2168 (1931).

weaker companions of the 4358 and 4046 mercury lines. The fact that the violet mercury lines themselves are not visible in the plates from which the data for the blue excitation are taken removes the possibility of error from this source in assigning origins to the Raman lines. This is of great importance in the region of 12–1400 cm^{-1} displacement. Fig. 5 shows the photographs obtained.

The values recorded are averages from several plates in most cases. In Tables I–V, the wave numbers of observed lines are given in the first

TABLE I. *n-butane.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
24479	*a*	5*b*	2909	22557	*g*	1*b*	438	21741	*d*	4	2964
24457	*a*	8*b*	2931	22510	*h*	3	428	21645	*h*	1*b*	1293
24422	*a*	5*b*	2966	22150	*h*	2	788	21640	*e*	1	2876
24356	*c*	3	2937	22105	*h*	6	833	21609	*e*	0	2907
	d		349	22045	*d*	0	2660	21580	*e*	2	2936
24282	*d*	2	423	22002	*d*	1	2703	21488	*h*	3*b*	1450
23916	*d*	2	789	21987	*h*	1	951	20268	*h*	0	2670
23877	*d*	4	828	21967	*d*	1	2738	20236	*h*	0	2702
23748	*d*	0	957	21958	*h*	2	980	20199	*h*	1	2739
23729	*d*	1	976	21880	*h*	3	1058	20074	*h*	5	2864
	e		787	21868	*h*	0	(1070)	20059	*h*	10	2879
23689	*e*	0	827	21843	*d*	5	2862	20026	*h*	3	2912
23649	*d*	2	1056	21826	*d*	10	2879	19997	*h*	8	2941
23557	*d*	1	1148	21794	*d*	4	2911	19975	*h*	3	2963
23252	*d*	4*b*	1453	21789	*h*	1	1149				
22600	*h*	0	(338)	21766	*d*	10	2939				

(338) (0), 428 (3), 787 (2), 832 (6), 951 (1), 980 (2), 1058 (3), (1070) (0), 1149 (1), 1293 (1*b*), 1450 (3*b*), 2670 (0), 2702 (0), 2739 (1), 2864 (5), 2879 (10), 2912 (3), 2941 (8), 2963 (3).

TABLE II. *Chlorobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
24307	*a*	1	3081	23235	*d*	0	1470	21780	*h*	3	1158
24287	*d*	2	418		*h*		−297	21763	*h*	2	1175
24091	*d*	2*b*	614	23119	*d*	1	1586	21700	*d*	0	3005
	e		425	22740	*h*	7	198	21678	*d*	0	3027
24001	*d*	5	704	22663	*h*	0	275	21637	*d*	10*b*	3068
23964	*d*	0	741	22639	*h*	2	299	21614	*h*	0	1324
23962	*h*	1	−1024	22607	*h*	0	331	21572	*h*	0	1366
23938	*h*	1	−1000	22580	*g*	1	415	21564	*d*	0	(3141)
23813	*e*	1	703	22520	*h*	6	418	21539	*d*	0	3166
23702	*d*	5	1003	22473	*h*	1	465	21536	*h*	0	(1402)
23680	*d*	2	1025	22380	*g*	0	615	21500	*h*	1	1438
23618	*d*	2	1087	22324	*h*	3	614	21459	*h*	1	1479
23581	*d*	1*b*	1124	22294	*g*	1	701		*f*		1580
23549	*d*	0	1156	22236	*h*	5	702	21447	*e*	2	3069
23530	*d*	0	1175	22196	*h*	1	742	21410	*g*	1	1585
23512	*e*	1	1004	22108	*h*	2*b*	830	21377	*h*	1	1561
23491	*e*	1	1025	22035	*f*	1	1004	21354	*h*	6	1584
23430	*e*	1	1086	21993	*g*	2	1002	20609	*h*	0	(2329)
23352	*e*	2	1164	21973	*g*	1	1022	19869	*h*	2	3069
	h		−414	21935	*h*	10	1003	18110	*k*	3	198
23336	*d*	0	1369	21915	*h*	7	1023	18005	*k*	1	303
	e		1180	21854	*h*	5	1084	17907	*k*	5	401
23260	*d*	0	1445	21817	*h*	2	1121	17697	*k*	2	611
								17317	*k*	1	991

198 (7), 275 (0), 299 (2), 331 (0), 419 (6), 465 (1), 614 (3), 703 (5), 743 (1), 832 (2), 1004 (10), 1023 (7), 1084 (5), 1122 (2), 1159 (3), 1174 (2), 1324 (0), 1366 (0), (1402) (0), 1438 (1), 1475 (1), 1561 (1), 1584 (6), (2329) (0), 3005 (0), 3027 (0), 3069 (10), (3141) (0), 3166 (0).

TABLE III. *Bromobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
24388	*d*	3	317	22622	*h*	10	316	21496	*h*	1	1442
24286	*b*	0*b*	3067	22585	*h*	1*b*	353	21461	*h*	1	1477
24229	*a*	1*b*	3159	22323	*h*	3	615		*f*		1578
	c		3064		*g*		672	21453	*e*	3	3063
24199	*e*	2	317	22265	*h*	5	673	21415	*g*	1	1580
24089	*d*	2	616	22200	*h*	1	738	21362	*e*	1	3154
24032	*d*	3	673	22143	*h*	0	795	21358	*h*	5*b*	1580
23869	*d*	0	(836)	22107	*h*	1	831	21324	*h*	0	1614
23840	*e*	1	676	22035	*f*	1	1004	21271	*h*	0	1667
23701	*d*	10	1004	22018	*f*	0	1021	20645	*h*	0	2293
23681	*d*	6	1024	21994	*g*	3	1001	20605	*h*	0	2333
23631	*d*	5	1074	21972	*g*	1	1023	19876	*h*	3	3062
23542	*d*	1*b*	1163	21936	*h*	10	1002	18974	*k*	0	−666
23527	*d*	1	1178	21915	*h*	5	1023	18559	*k*	1	(−251)
23512	*e*	2	1004	21866	*h*	4	1072	18123	*k*	2	185
23491	*e*	1	1025	21834	*g*	0*b*	1161	18044	*k*	0	264
23443	*e*	1*b*	1073	21778	*h*	3	1160	17989	*k*	3	319
23253	*d*	1*b*	1452	21761	*h*	2	1177	17315	*k*	6	993
23248	*h*	1*b*	−310	21701	*d*	0	3004	17292	*k*	1	1016
23124	*d*	4*b*	1581	21664	*h*	0*b*	(1274)	17250	*k*	1	1058
23113	*h*	1	−175	21640	*d*	10*b*	3065				
22753	*h*	8*b*	185	21637	*h*	0	1301				
22719	*f*	1	320	21616	*h*	0	1322				
22681	*h*	2*b*	257	21553	*d*	1	3152				
	g		314	21502	*d*	0	3203				

185 (8*b*), 260 (1*b*), 317 (10), 353 (1*b*), 616 (3), 673 (5), 738 (1), 795 (0), 831 (1), 1002 (10), 1023 (5), 1072 (4), 1160 (3), 1177 (2), (1274) (0), 1301 (0), 1322 (0), 1442 (1), 1477 (1), 1580 (5*b*), 1614 (0), 1667 (0), 2293 (0), 2333 (0), 3004 (0), 3063 (10), 3153 (1), 3203 (0).

TABLE IV. *Iodobenzene.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
24437	*d*	2	268	22671	*h*	10	267	21500	*h*	1	1438
24247	*e*	1	269	22623	*h*	0	315	21469	*h*	1	1469
24090	*d*	0*b*	615	22550	*h*	0*b*	(388)		*f*		1570
24048	*d*	2	657	22383	*g*	0	612	21458	*e*	1	3058
23966	*d*	0	739	22324	*h*	2*v*	614	21425	*g*	0*b*	1570
23904	*e*	0	612		*g*		671	21365	*h*	5	1573
23859	*e*	0*b*	657	22282	*h*	5	656	21323	*h*	0	1615
23704	*d*	6	1001	22210	*h*	1	728	21278	*h*	0	1660
23685	*d*	4	1020	22100	*h*	1*b*	838	20612	*h*	0	(2326)
23640	*d*	1*b*	1065	22037	*f*	2	1002	19943	*h*	0	(2995)
23586	*h*	1	−648	22028	*f*	1	(1011)	19878	*h*	1	3060
23544	*d*	1*b*	1161	21995	*g*	3	1000	18565	*k*	2	−257
23514	*e*	2*b*	1002	21976	*g*	2	1019	18146	*k*	3*b*	162
23497	*e*	1	1019	21938	*h*	10	1000	18080	*k*	1	228
23454	*e*	0	1062	21919	*h*	6	1019	18039	*k*	5	269
23353	*e*	1	1163	21878	*h*	2	1060	17693	*k*	1*b*	615
23329	*e*	1	1187	21845	*g*	0*b*	1150	17652	*k*	4	656
23263	*d*	0	1442	21780	*h*	3	1158	17316	*k*	7	992
	g		−268	21759	*h*	2	1179	17295	*k*	3	1013
23231	*d*	1	1474	21702	*d*	0*b*	3003	17154	*k*	1*b*	1154
23200	*h*	3	−262	21681	*h*	0	1257	16735	*k*	3	1573
23130	*d*	2	1575	21647	*d*	10*b*	3058	15248	*k*	8	3060
23103	*h*	1	−165	21619	*h*	1	1319	15175	*k*	1	3163
22770	*h*	5*b*	168	21579	*h*	0	1359				
22720	*h*	3*bv*	218	21564	*d*	1	3141				

168 (5), 228 (2), 268 (10), (319) (0), (388) (0), 614 (2), 656 (5), 728 (1), 838 (1), 1001 (10), 1019 (6), 1062 (2), 1158 (3), 1179 (2), 1257 (0), 1319 (0), 1359 (0), 1440 (1), 1472 (1), 1573 (5), 1615 (0), 1660 (0), (2326) (0), (3000) (0), 3059 (10), 3141 (1).

TABLE V. *Alpha-chloropyridine.*

$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	I	$\Delta\bar{\nu}$
24388	*d*	0	(317)	23246	*d*	0	(1459)	21890	*h*	8	1048
24272	*d*	1	433	23130	*d*	2*b*	1575	21852	*h*	3	1086
24084	*d*	1	621	23113	*h*	1	−175	21817	*h*	3	1121
23976	*d*	2	729	22744	*h*	8	194	21784	*h*	2	1154
23796	*e*	0	720	22621	*h*	1	317	21698	*h*	1	1240
23708	*d*	4	997	22564	*g*	1	431	21650	*h*	2	1288
23655	*d*	3	1050	22509	*h*	8	429	21648	*d*	10	3057
23615	*d*	1*b*	1090	22318	*h*	4	620	21625	*d*	6	3080
23582	*d*	1*b*	1123	22270	*g*	0*b*	725	21577	*h*	0	(1361)
23550	*d*	1	1155	22210	*h*	3	728	21573	*d*	1*b*	3132
23519	*e*	1	997	22160	*h*	1	778	21544	*d*	0	(3161)
23466	*e*	1	1050	22052	*d*	1	2653	21512	*h*	0	(1426)
23414	*d*	0*b*	1291	22046	*f*	1*b*	993	21478	*h*	0	(1460)
23268	*h*	0	(−330)	22002	*g*	1	993	21463	*e*	1	3053
				21981	*d*	1	2724	21439	*e*	1	3077
				21967	*h*	1	971	21366	*h*	5	1572
				21945	*h*	10	993	19851	*h*	2*b*	3087

194 (8), 317 (1), 429 (8), 620 (4), 728 (3), 778 (1), 971 (1), 993 (10), 1048 (8), 1086 (3), 1121 (3), 1154 (2), 1240 (1), 1288 (2), (1361) (0), (1426) (0), (1460) (0), 1573 (5), 2653 (1), 2724 (1), 3057 (10), 3080 (6), 3132 (1), (3161) (0).

column, symbols for the exciting line in the second, the intensity and character of the line in the third, and the displacement assigned to it in the fourth. The symbols for the exciting lines are taken from Kohlrausch.[3]

a 27388 cm^{-1}	*d* 24705	*f* 23039	*k* 18308
b 27353	*e* 24516	*g* 22995	
c 27293		*h* 22938	

The intensities given are merely visual estimates of the relative blackness of the lines and are not strictly comparable from one substance to another. The letter *b* signifies broad, *v* shaded to the violet, and *r* shaded to the red. The values appearing in parentheses in the body of the tables are uncertain due to extreme weakness or interference of background. Those in parentheses in the summaries are uncertain from the above causes or on account of doubt as to their origin.

The Raman frequencies are summarized at the end of each table and the intensities are given in parentheses after the displacements. The values are probably accurate to within 3 cm^{-1} or better for the stronger lines but the error for the very weak ones may be as large as 10 cm^{-1}. The plates were measured on a Gaertner comparator and the wave numbers determined from a large dispersion curve constructed from an iron comparison spectrum. The accuracy of the lines excited by the green line is less on account of the low dispersion in that region.

III. DISCUSSION

The results reported here for *n*-butane confirm those of Bhagavantam except that the line he reported at 960 has been resolved into two lines at 951 and 980. The lines at 320 and 1067 were not well substantiated in this work though traces of them were found.

Dadieu and Kohlrausch[8] reported a line for chlorobenzene at 484 in their first paper on this substance but did not report it in a later paper in which the work was repeated.[9] A line has been found at 465 which might be the one in question considering the error in measurement of such weak lines. The line at 3133 reported in the latter paper was not substantiated in this work though a trace of it was found. All other previously reported lines have been confirmed. New lines have been found at: 275, 331, 1174, 1324, (1402), 1438, 1475, 1561, (2329), 3005, 3027. The justification for the assignment of a line to 1475 is not apparent from the table and is based on the fact that the observed line at 21459 cm^{-1} is stronger than the line at 21410 which would not be the case if the former were due to the 1584 line excited by the 4339 line alone. This same reasoning applies to the other compounds in which this line is found.

[8] Dadieu and Kohlrausch, Monats. f. Chem. **52**, 379 (1929).

[9] Dadieu, Kohlrausch and Pongratz, Monats. f. Chem. **61**, 426 (1932).

In the case of bromobenzene, Fujioka[6] reports a line at 222 which is derived from the observed line at 22716 and is assumed to have been excited by the 4358(*h*) mercury line. A similar line was found in the present work but it was deemed more probable that it was excited by the 4348(*g*) mercury line and is so reported in this paper. The line at 1370 reported by Dadieu and Kohlrausch was not found though several other weak lines were found in this region. The resolution of the strong line at 3063 into two lines reported by Fujioka was not satisfactorily confirmed though a trace of it was found in one plate. In other respects, the previously reported lines have been confirmed. New lines have been found at: 353, 738, 795, 831, 1274, 1301, 1322, 1442, 1477, 1614, 1667, 2293, 2333, 3004, and 3203.

In the case of iodobenzene, a line at 462 was reported by Dadieu and Kohlrausch[8] in the earlier paper but was not reported by them in a later paper.[10] This line was not found in the present work. All other previously reported lines have been found. New lines have been found at: 228, 319, 388, 728, 838, 1179, 1257, 1319, 1359, 1440, 1472, 1615, 1660, (2326), (3000) and 3141. The line at 228 is not distinguishable from the 268 line excited by 4348(*g*) when excited by the 4358(*h*) line and is masked by the mercury radiation when excited by the violet line. For this reason, its identity has not been established before though the line has been observed. This question has been settled by excitation with the green line. The incompleteness of the previous work on this substance is largely due to the decomposition caused by ultraviolet light. This difficulty has been overcome by protecting it with sodium nitrite.

The marked similarity between the monohalogen derivatives of benzene is very evident from Figs. 4 and 5. Nearly all of the lines which do not correspond throughout the series are so weak that they may well have been missed in the cases where they are absent. The line at 1122 in chlorobenzene appears to be missing in the bromo and iodo compounds; but this is not certain for it may coincide with the position of the 1159 line excited by 4348(*g*). In this case, however, the intensity must have fallen off sharply. The weak companion of the 1584 line in chlorobenzene is not found in the other compounds but two very weak lines appear on the other side of it at 1615 and 1660.

The lines at 198, 299, 419, 465 and 703 in chlorobenzene move toward the exciting line by very appreciable amounts in passing to the bromo and iodo compounds and thus appear to correspond to motions in which the carbon to halogen bond plays an important part. The lines at 614, 832, 1004, 1023, 1159, 1174, 1438 and 1475 remain nearly constant and hence pertain to motions in which this bond is not very much involved. The lines at 743, 1084, 1584, 3069 and 3166 are very slightly lowered on increasing the mass of the substituent and thus appear to involve this bond to a slight extent. The remainder of the lines are so weak that too much confidence should not be placed in apparent shifts though the lines in the region of 1200 to 1400 appear to have a genuine shift to lower values. It is of interest in connection with the lines at about 2300 that a line at 2291 has recently been found for benzene by Wood and Collins.[11]

Many of the new lines found for the benzene derivatives are of particular interest in that they were predicted by Mr. D. E. Teets of this laboratory from studies of the vibrating mechanical models which will be published in the near future.

The obvious similarity of the spectra of chlorobenzene and alpha-chloropyridine would appear to indicate that the ring structures of the two compounds are of the same type.

[10] Dadieu and Kohlrausch, Monats. f. Chem. **57**, 488 (1931).

[11] Wood and Collins, Phys. Rev. **42**, 382 (1932).

The Free Energy of Ozone[1]

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The infrared spectrum of ozone is discussed. Gerhard's three fundamental frequencies, 528 cm^{-1}, 1033 cm^{-1}, and 1355 cm^{-1} are shown to be in somewhat imperfect agreement with experiment. They are nevertheless sufficiently reliable to justify a spectroscopic calculation of the free energy of ozone, in view of the unreliability of the experimental data. Ozone is found to be much less stable than experiment had shown; $S_{298.1}=57.0$ cal./deg./mole, as compared with $S_{273}=86.5$ based on e.m.f. measurement. The maximum partial pressure of O_3 in an equilibrium mixture of O, O_2, and O_3 at a total pressure of 1 atm. is 1.0×10^{-6} atm. at 3400°K. The 1 percent ozone obtained by heating filaments to 2300°K in liquid oxygen must have been formed in the cold regions from atomic oxygen.

ABOUT thirty years ago, strenuous efforts were made to determine the free energy of ozone. The various e.m.f. measurements which were attempted met with the general difficulties that the electrode reactions were not known and not reversible.[3] Many attempts to detect ozone in very rapidly cooled oxygen failed. When it was realized that the high rate of decomposition of ozone even at 200° doomed such experiments in advance, Fischer and Braehmer[4] burnt hydrogen, carbon monoxide, and other gases under liquid air or oxygen, and also heated Nernst filaments in liquid oxygen. They obtained in this way solutions of ozone in concentration up to 1 percent; this represents an upper limit to the equilibrium concentration at the filament temperature (2300°K) since there may have been a considerable fractionation effect as the oxygen evaporated. It will be seen from what follows that the ozone found in this work must have been formed almost entirely from atomic oxygen, and that no experiment of this sort can possibly give the equilibrium concentration of ozone. Recently, Wulf[5] has decided that an empirically estimated entropy value is more reliable than the very high values given by the foregoing experiments.

The existing spectroscopic data for ozone are rather scanty, but they seem to be sufficient to yield entropy and free energy values far superior to those available from any other source. The early work on its infrared absorption[6] showed bands at 1.1, 3.7, 4.8, 6.6, 7.6, 9.9, and 11.35μ. Recently, Gerhard[7] has examined the 4.7, 7.39, 9.6, and 11.38μ bands with a high-dispersion grating spectrometer; the resolution was apparently just insufficient to yield individual lines. The 4.7μ (2108 cm^{-1}) and 7.39μ (1355 cm^{-1}) bands show a strong zero branch. The band at 9.6μ is apparently complex, with a zero branch band at 9.47μ (1055 cm^{-1}) superimposed on a doublet band at 9.67μ (1033 cm^{-1}). The weak band at 11.38μ shows a single peak. Since it does not resemble the others, and does not fit the frequency scheme, it is tentatively assigned to nitrogen pentoxide by Gerhard; the method of preparation used is such as to make this impurity relatively unlikely. Gerhard adopts the three fundamental frequencies 528 cm^{-1}, 1033 cm^{-1}, and 1355 cm^{-1}, as ν_2, ν_3 and ν_1, respectively. The experimental conditions did not permit study in the region of ν_2. The appearance of the bands suggests rather definitely that there are three different moments of inertia. It is therefore reasonable to consider the molecule an isosceles triangle. For this case the three normal modes of vibration have different frequencies. Analysis

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[3] Jahn, Zeits. f. anorg. Chem. **60**, 332 (1908).

[4] Fischer and Braehmer, Ber. **39**, 940 (1906).

[5] Wulf, J. Am. Chem. Soc. **54**, 156 (1932).

[6] Ladenburg and Lehman, Ann. d. Physik **21**, 305 (1906); Warburg and Leithauser, ibid. **23**, 209 (1907); **28**, 313 (1909).

[7] Gerhard, Phys. Rev. **42**, 622 (1932).

shows[8] that in two of them (ν_1 and ν_2, according to the convention adopted) the electric moment vibrates along the Y axis (the symmetry axis) and for ν_3 perpendicular to this axis. Now Dennison[9] has shown that when the electric moment moves along the least moment of inertia, the bands show a zero branch; when it moves along the middle moment of inertia, a doublet structure. Thus, if the three fundamental frequencies have been correctly selected, the assignment made by Gerhard supposes that the 528 cm^{-1} band will show a zero branch, and that the triangle has an apex angle less than 60°. If 528 cm^{-1} has a doublet structure we would have to take $\nu_1=1033$ cm^{-1}, $\nu_2=528$ cm^{-1}, and $\nu_3=1355$ cm^{-1}. The middle moment of inertia would lie along the figure axis, and the apex angle would be greater than 60°. The 1055 cm^{-1} band, which is assigned to $2\nu_2$, should then show a doublet structure, instead of a zero branch. We cannot consider 1055 cm^{-1} a fundamental, and 1033 cm^{-1} the overtone of 528 cm^{-1}; for if we did, 528 cm^{-1} by elimination would become a doublet, and ν_3. But, in view of the alternation shown by Dennison to exist for ν_3, $2\nu_3$ would be a zero branch, in contrast to the observed structure. Thus, if the three fundamental frequencies have been correctly selected, there seems to be no alternative to Gerhard's assignment of them, and his conclusion that the apex angle is less than 60°. There is certainly no obvious way in which different fundamentals can be selected.

The comparison of these frequencies with the theoretical ones for a simple model, however, is not very satisfactory. We take for the potential energy

$$(1/2)(Kx_{12}^2+K'x_{13}^2+K'x_{23}^2),$$

where x_{ij} is the relative displacement of atoms i and j; the apex atom is numbered 3. It can then be shown that of the three possible assignments of the observed fundamentals to the different modes of vibration, only the one made by Gerhard gives a real solution. It gives two solutions: for one the apex angle is 59° 16′, $K/K'=0.2198$, and the ratio of least to middle moment of inertia is 0.9706; for the other, the apex angle is 117° 16′, $K/K'=1.662$, and the ratio of least to middle moment of inertia is 0.1245. Reference to the diagrams given by Dennison shows that for the former case the separation into zero and doublet bands would not have developed to a noticeable extent, while for the latter case the doublet bands would have a very coarse structure; neither case corresponds well with the observed structures. Furthermore, the ratio K/K' in both cases has an unexpected value.[10]

Jakowlewa and Kondratjew[11] have measured some of the ultraviolet bands of ozone. They propose frequencies different from those of Gerhard, and favor a linear form for the molecule. Consideration, however, shows that their data are not well suited to analysis. The bands are not located with a certainty of better than 5 cm^{-1}, and there are so many bands that the chance coincidences outnumber the real ones several fold.

The following calculations have been based on Gerhard's frequencies. The symmetry number is taken as two, in agreement with his conclusion. The value for the moment of inertia has been computed, assuming O–O distances of 1.2, 1.4 and 1.4×10^{-8} cm. It is unlikely that the error in F because of a possible incorrect assignment of the frequencies exceeds 500 cal. at 1000°K, 2500 cal. at 2000°K or 5000 cal. at 5000°K. We assume harmonic oscillators; the resulting error in F is perhaps 1000 cal. at 5000°K. The only other value for the symmetry number which seems at all possible is three. The product of the three moments of inertia will scarcely be wrong by more than 25 percent, unless the apex angle is considerably greater than 120°, and the ratio of least to middle moment of inertia less than 0.1; as has been pointed out, the appearance of the bands is against this. We assume that the

[8] Dennison, Phil. Mag. **1**, 195 (1926).
[9] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[10] Since this paper was written, Badger and Bonner, Phys. Rev. **43**, 305 (1933), have criticized Gerhard's frequency assignment on grounds very similar to those mentioned above. On this basis, and with reference to Wulf's analysis of certain electronic bands, Proc. Nat. Acad. Sci. **16**, 507 (1930), they favor $\nu_1=1050$, $\nu_2=440$ and $\nu_3=1355$ cm^{-1}. These frequencies do give one reasonable solution, an apex angle of 81° 0′ with $K/K'=0.619$. The agreement with the infrared bands is definitely less good than that of Gerhard's assignment, but the existing data scarcely justify a definite decision.

[11] Jakowlewa and Kondratjew, Phys. Zeits. d. Sow. **1**, 471 (1932).

TABLE I. *Free energies, equilibrium constants and equilibrium concentrations for ozone.*

Temp. (°K)	$-(F^0-E_0^0)/T$ for O_3	Log$_{10}$ K		Equilibrium partial pressure at 1 atm. total pressure		
		$K=\frac{(O_2)^{\frac{3}{2}}}{(O_3)}$	$K=\frac{(O_2)(O)}{(O_3)}$	O_2	O	O_3
250	47.121	——	——	——	——	——
298.1*	48.558	28.490	−11.899	1.000	4.0×10^{-41}	3.2×10^{-29}
300	48.828	28.285	−11.829	1.000	7.8×10^{-41}	5.2×10^{-29}
350	49.972	24.793	− 9.150	1.000	1.1×10^{-34}	1.6×10^{-25}
400	51.142	22.149	− 7.159	1.000	5.0×10^{-30}	7.1×10^{-23}
450	52.200	20.092	− 5.606	1.000	2.0×10^{-26}	8.1×10^{-21}
500	53.167	18.447	− 4.341	1.000	1.6×10^{-23}	3.6×10^{-19}
550	54.061	17.101	− 3.338	1.000	3.6×10^{-21}	7.9×10^{-18}
600*	54.890	15.980	− 2.484	1.000	3.4×10^{-19}	1.0×10^{-16}
700	56.408	14.214	− 1.144	1.000	4.4×10^{-16}	6.1×10^{-15}
800	57.759	12.891	− 0.128	1.000	9.6×10^{-14}	1.3×10^{-13}
900	58.992	11.858	+ 0.659	1.000	6.4×10^{-12}	1.4×10^{-12}
1000	60.116	11.031	+ 1.291	1.000	1.8×10^{-10}	9.3×10^{-12}
1250	62.573	9.541	+ 2.431	1.000	7.8×10^{-8}	2.9×10^{-10}
1500	64.689	8.537	+ 3.186	1.000	4.4×10^{-6}	2.9×10^{-9}
1750	66.533	7.816	+ 3.724	1.000	7.8×10^{-5}	1.5×10^{-8}
2000	68.073	7.291	+ 4.148	0.999	7.2×10^{-4}	5.1×10^{-8}
2500	70.812	6.536	+ 4.722	0.985	0.015	2.9×10^{-7}
3000	73.096	6.032	+ 5.108	0.888	0.112	7.8×10^{-7}
4000	76.777	5.400	+ 5.595	0.237	0.763	4.6×10^{-7}
5000	79.687	5.022	+ 5.894	0.017	0.983	2.2×10^{-8}

* The equilibrium constants for $O_2=2$ O and the percentage dissociations given by Johnston and Walker at 298.1° and 600° are incorrect; their $(F^0-E_0^0)/T$ values, however, are apparently correct at these temperatures. The method of graphical interpolation they have used to obtain $(F^0-E_0^0)/T$ at intermediate temperatures is apparently less accurate than the procedure of Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932), but is good enough for the purposes of the present paper.

normal state is $^1\Sigma$ and that there are no other electron levels low enough to require consideration; this may be incorrect. Some of these errors would increase the equilibrium concentration of ozone, others decrease it. The calculated values are probably correct within a factor of two, and certainly within one of five. They may be much better than this, but at the worst are a great deal better than any experimental results.

The heat of formation of one mole of ozone at constant volume is given as $-34{,}220\pm180$ cal., by the recent work of Gunther, Wassmuth and Schryver.[12] From this we calculate that $\Delta E_0^0=34{,}513$ cal.

The methods used in the calculations have been given in a previous article.[13] The entropy of ozone at 25°C is found to be 57.0 cal./mole/deg. This is somewhat higher than the estimate of 52.6 made by Wulf, but much lower than the old value of $S_{273}=86.5$ based on e.m.f. measurements.

Table I gives the $(F^0-E_0^0)/T$ values for ozone, the equilibrium constants for $O_3=(3/2)O_2$ and for $O_3=O_2+O$, and the partial pressures of O, O_2 and O_3 at equilibrium at a total pressure of 1 atm. These latter values are also shown in Fig. 1. The $(F^0-E_0^0)/T$ values for O and O_2 are taken from Johnston and Walker.[14] The values for O_2 do not take account of the low-lying $^1\Delta$ state predicted by Mulliken[15] and Hückel,[16] and confirmed by specific heat measurements.[17] The inclusion of this level would make O_2 more stable with respect to all reactions. An approximate correction has been made for this level, and the new equilibrium values have been calculated. The curves for O and O_2 are not shifted enough to show in Fig. 1; the ozone curve is lowered somewhat, but the effect is not large. In view of what has been said

[12] Gunther, Wassmuth and Schryver, Zeits. f. physik. Chemie **A158**, 297 (1932).

[13] Kassel, J. Am. Chem. Soc. **55**, 1351 (1933).

[14] Johnston and Walker, J. Am. Chem. Soc. **55**, 172, 187 (1933).

[15] Mulliken, Phys. Rev. **32**, 186 (1928).

[16] Hückel, Zeits. f. Physik **60**, 442 (1930).

[17] Lewis and von Elbe, Phys. Rev. **41**, 678 (1932).

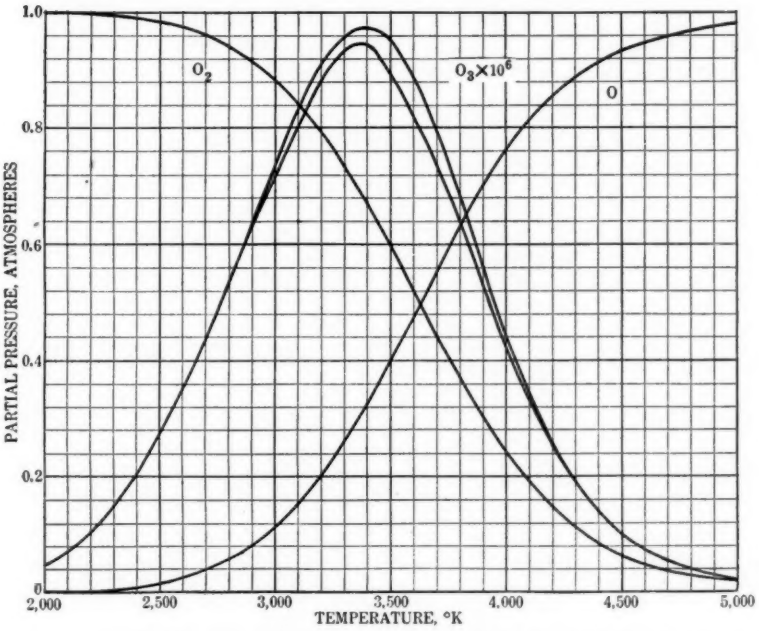

FIG. 1. Equilibrium partial pressures of O, O_2 and O_3 at 1 atm. total pressure. The upper curve for ozone is based on the $(F^0-E_0^0)/T$ values for oxygen given by Johnston and Walker; the lower curve includes an approximate correction for the $^1\Delta$ state of oxygen; both ozone curves should be raised by an amount ranging from 7.6 percent at 2000° to 3.1 percent at 5000°, to correspond with the values of Table 1; such a shift is considerably less than the probable error of the values.

previously with regard to possible errors, it is clear that there is no temperature at which the ozone partial pressure is as much as 5×10^{-6} atm., at a total pressure of 1 atm. The ozone found by Fischer and Braehmer must have been formed from atomic oxygen, for which the equilibrium concentration at 2300°K is 0.0052, comparing favorably with their estimate of 1 percent ozone. The calculations also show that there is no ozone contribution to the apparent specific heat of oxygen at high temperatures, and thus make it more certain that Lewis and von Elbe were justified in associating the observed increase of specific heat with excitation to the $^1\Delta$ level of O_2.

It has not seemed worth while to tabulate the other thermodynamic functions; quite good values for H and S may be obtained by graphical or analytical differentiation; a very satisfactory procedure is to fit F/T at three successive temperatures to $F/T=A+B\ln T+C/T$. This same equation will give specific heats good to about 0.5 cal./deg. The only reason for giving F/T and $\log K$ to three decimal places is to permit such calculations as these, which could not be made if fewer were given.

The Mechanism of Substitution Reactions

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For many substitution reactions of the type $AB+C \rightarrow AC+B$, the strength of the bond between A and B is too great to account for the rate of the reaction. For such reactions addition or simultaneous addition and dissociations must occur. From the quantum mechanical conception of bonds, it is shown that a spatial inversion of A occurs for every such substitution. This theory is applied in detail to some experiments on the Walden inversion, and a definite correlation between rotational and configurational changes is obtained. Its use is studying molecular rearrangements and cis-trans isomerization is sketched.

THE assumption that all substitution reactions, $AB+C \rightarrow AC+B$, can be divided into two mutually exclusive classes, i.e., (1) those in which dissociation of AB is the primary step, and (2) those in which the formation of the complex ABC is the primary step, is predicated on the postulate that each type of atom or molecule can be characterized by a definite size. However, dissociation and association are not instantaneous events, but are processes which require finite time, and therefore we must regard the above classes as limiting cases of a more inclusive group in which dissociation and association may be simultaneous phenomena.

The transition from the ordinary addition product to the simultaneous association and addition can be illustrated by the gaseous reactions

$$Cl_2+Cl \rightarrow Cl_3 \rightarrow Cl_2+Cl, \quad (1)$$

$$H_2+H \rightarrow H_3 \rightarrow H_2+H, \quad (2)$$

$$H_2+Br \rightarrow H_2Br \rightarrow HBr+H. \quad (3)$$

For all of these reactions, the heats of dissociation of the diatomic molecules is so large that in each case we can neglect primary dissociation.

Rollefson and Eyring[1] have applied the theory developed by London[2] to reaction (1). They found that 4.5 kilocalories activation energy was required to form the addition product, and 8.6 kilocalories was required to dissociate it. Furthermore the separation of the chlorine atoms in the original molecule increased only very slightly as the third atom approached. We would therefore be justified in assuming that in this case addition preceded dissociation.

For the hydrogen reaction Farkas[3] found that atomic hydrogen was a catalyst for the conversion of para hydrogen into ortho hydrogen. London's theory was applied to this reaction by Eyring and Polanyi.[4] They found that it required an activation energy of 11 kilocalories. They showed also that as the hydrogen atom approaches the molecule along the molecular axis, the atoms composing the original molecule begin to separate. The molecule H_3 needs about 1.5 kilocalories to decompose it, and so here again an addition compound could exist, but to a much more limited extent than in the chlorine case.

For the third reaction, the formation of an addition compound in the ordinary sense is impossible for the potential energy diagram of the reaction shows no region of stability for H_2Br. We are, therefore, dealing with simultaneous dissociation and addition. This evanescent addition product has this, however, in common with its more stable prototypes: The system requires much less activation energy if the bromine atom approaches the hydrogen molecule along the molecular axis than if it approaches it from any other direction.

[1] G. K. Rollefson and H. Eyring, J. Am. Chem. Soc. **54**, 170 (1932).

[2] F. London, Zeits. f. Elektrochemie **35**, 552 (1929).

[3] L. Farkas, Zeits. f. physik. Chemie **B10**, 419 (1930).

[4] H. Eyring and M. Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).

In the simple systems which we have considered, experimental proof of this statement cannot be obtained, but if the theory is extended to reactions such as

$$AB+C^-\rightarrow AC+B^-$$

$$AB+C\rightarrow AC+B$$

$$AB+C^+\rightarrow AC+B^+$$

where A in particular may be a complex radical, we will be forced to certain conclusions, some of which can be subjected to experimental test. The strict application of London's theory to such complex systems is out of the question. Not only are important data lacking, but the calculations involved in a quantitative solution of the problems are, at the present time, hopelessly burdensome. We can, however, get a qualitative picture from the type of potential energy diagram that would be expected for certain changes in the system. Thus let AB be the molecule $R_1R_2R_3CCl$ in which the bonds between the R's and C are strong enough so that Cl can be identified with B. By plotting the energy of the system, ϵ, against the distance separating $R_1R_2R_3C$ from Cl (or between the corresponding ions) we obtain a curve of the type shown in Fig. 1, where r_0 is the equilibrium separation

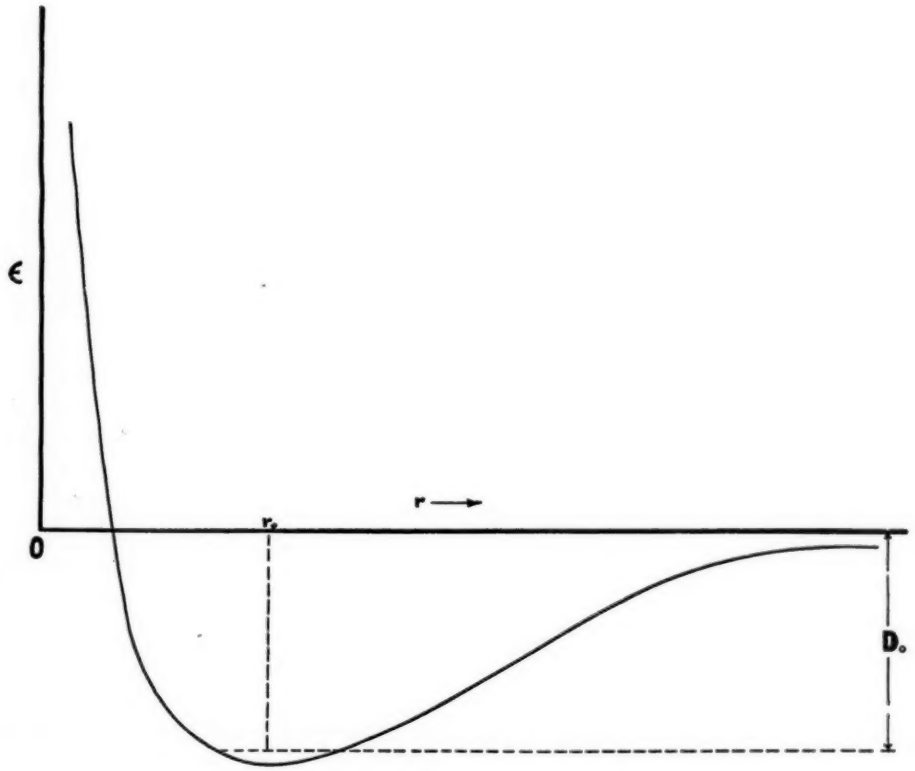


FIG. 1. Type of potential energy curve for the dissociation of $R_1R_2R_3CX$ into $R_1R_2R_3C$ and X, or into the corresponding ions.

According to Pauling[5] the average value of D_0 for the carbon chlorine bond in substituted hydrocarbons is about 80 kilocalories per mol. This refers, however, to dissociation into a neutral atom and a radical. For dissociation into ions, D would be almost twice as much due to the difference between the ionizing potential of the radical and the electron affinity of chlorine. If the substance is in solution, cor-

[5] L. Pauling, J. Am. Chem. Soc. 54, 3570 (1932).

rections for hydration and the dielectric constant of the solvent would have to be applied. This latter correction may be much smaller than is ordinarily supposed, for most of the work of separation is done at very small distance and here the effective dielectric constant seems to approach unity, as is shown by the fact that the frequencies of Raman lines are almost independent of the nature of the solvent. Fortunately for those substances which are to be discussed, we were able to obtain experimental[6] proof of the assumption of a large value of the heat of dissociation into ions, not only for some chlorine compounds, but also for some bromine compounds. According to the Arrhenius equation, the speed of a reaction in which dissociation is a primary step is proportional to $e^{-D/RT}$. In our experiments aqueous solutions of *d*-chlor succinic acid, and of *l*-phenyl brom acetic acid were prepared. To the first solution sulfuric acid was added and to the second perchloric acid was added. This was done to repress not only hydroxide ion, but also the ions of the halogen acids so as to reduce either inter- or intra-ionic addition. Sulfate ion and perchlorate ion are much less prone to form addition complexes than other negative ions as was shown by Brönsted, Kilpatrick and Kilpatrick.[7] This procedure does not eliminate all addition compounds for, as will be shown later, substances which have unbonded electron pairs can add. The chlor succinic acid solution was kept at 85°C for four hours and the phenyl brom acetic acid solution was kept at room temperature for five hours. In both cases the change in rotation was negligible, thus showing that primary dissociation does not occur to an appreciable extent. To this it might be objected that the free ions such as $C_6H_5C^+HCOOH$ retain their configurations, but were this the case, chloride and bromide ions could have no effect except to repress ionization. However, the racemizing action of these ions has been completely demonstrated not only in this laboratory, but also by Holmberg[8] and by Kekule.[9] The reaction of such compounds, therefore, cannot proceed by primary dissociation, and so we must assume an addition compound or simultaneous addition and dissociation.

The assumption of primary addition compounds in substitution reactions dates back at least to Kekule.[9] Both Fischer[10] and Werner[11] independently assumed addition reactions to explain the Walden inversion. Werner, furthermore, postulated simultaneous dissociation and addition. Both authors assumed that the entering group might or might not take the place of the dissociating group.

A more definite statement was made by Lewis.[12] "There seems to be but one possible way of accounting for this peculiar behavior (Walden inversion). Let us consider a carbon atom attached to the four radicals R_1, R_2, R_3 and R_4, and let us assume that a fifth group, R_5, becomes temporarily attached to the carbon atom near to the face of the tetrahedron which is opposite to R_1. A slight shift of the kernel might make it now the center of a new tetrahedron with corners at R_2, R_3, R_4 and R_5, while R_1 would become detached from the molecule. Then if the radical R_5, in the new molecule were to be replaced by the radical R_1, the resulting molecule would be the mirror image of the one with which we started. In this explanation it is not necessary to assume that the five radicals are attached to the carbon for any appreciable period of time, indeed it might be assumed that the R_1 leaves at the same instant that the R_5 becomes attached to the carbon atom."

Chemists and theoretical physicists agree that a molecule such as $R_1R_2R_3CCl$ should be represented as a tetrahedron. There is, however, this important difference; to most chemists the bond, i.e., the bond between carbon and chlorine, is thought of as extending between the carbon atom and the chlorine atom. But Pauling[13] and Slater[14] have shown by means of quantum mechanics that the carbon eigenfunction which is involved in the carbon chlorine bond extends beyond the

[6] The original experimental work mentioned in the various parts of this article will be published separately in collaboration with Miss M. J. Young and Mr. F. A. Long.

[7] J. N. Brönsted, Mary Kilpatrick and Martin Kilpatrick, J. Am. Chem. Soc. **51**, 428 (1929).

[8] B. Holmberg, J. prakt. Chem. **196**, 553 (1913).

[9] Kekule, Ann. Chem. **130**, 21 (1864).

[10] E. Fischer, Ann. **381**, 123 (1911).

[11] A. Werner, Ber. **44**, 873 (1911).

[12] G. N. Lewis, *Valence and the Structure of Atoms and Molecules*, p. 113, Chemical Catalog Company, N. Y., 1923.

[13] L. Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

[14] J. C. Slater, Phys. Rev. **37**, 481 (1931).

carbon atom on the side away from the chlorine. The carbon atom, therefore, has a tendency to form a bond at each face of the tetrahedron. The stronger the bond is to the apex, the weaker the bond-forming power is to the opposite face since the strength of a bond is related to the amount that the eigenfunctions overlap. It must also be remembered that the chlorine in such a compound has, to some extent, the negative characteristics of chloride ion, as is shown, not only by its eventual ejection from the molecule as chloride ion, but also by dipole measurements, x-ray diffraction pictures of dichlor ethane, etc. A particle with unbonded electron pairs such as a chloride or a hydroxide ion will therefore require a smaller energy of activation to react with $R_1R_2R_3CCl$ if it approaches the carbon face directly opposite to the chlorine. It is immaterial whether there is addition or simultaneous addition and dissociation. The important point is that the group which is to be displaced determines a unique path for the entering group, such that the system requires less energy than it would for any other path. This, then, leads to complete inversion of configuration for a reaction which takes place in one step.

Experimentally the existence of this face centered bond is indicated by the work of Menke.[15] In order to interpret the x-ray diffraction pattern of liquid carbon tetrachloride, Menke assumed a structure in the liquid in which a chlorine from one molecule of carbon tetrachloride was face centered on the adjoining carbon tetrachloride tetrahedron.

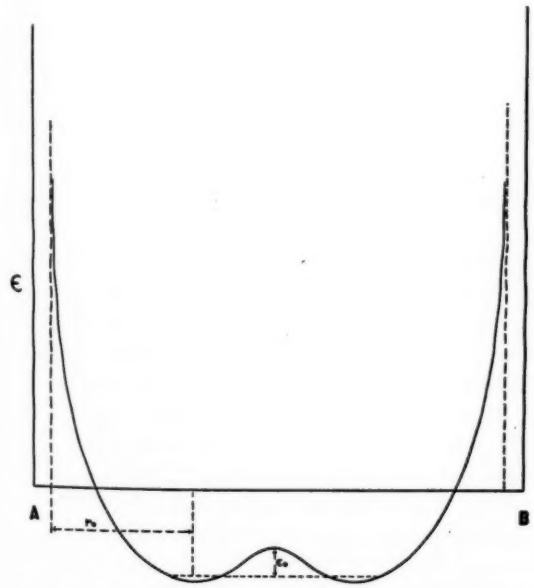


FIG. 2. Type of potential energy curve for the dissociation of $R_1R_2R_3CX$ into $R_1R_2R_3C$ and X, or into the corresponding ions in the presence of X or X ion.

The potential energy diagram of the system with the chloride ion added would be of the type shown in Fig. 2 where r_0 and ϵ_0 would depend on the distance AB separating the two chlorines. Some of these heats of activation for halogen acids and halide ions are now being measured in this laboratory. They are about 25 kilocalories per mol.

If there is more than one substance which can add we must consider sets of independent reactions. Thus in an aqueous solution of *l*-phenyl brom acetic acid, the initial reaction probably is

$$l\text{-}C_6H_5CHBrCOOH + OH^- \rightarrow d\text{-}C_6H_5CHOHCOOH + Br^-. \quad (4)$$

As the reaction proceeds the reaction

$$l\text{-}C_6H_5CHBrCOOH + Br^- \rightarrow d\text{-}C_6H_5CHBrCOOH + Br^- \quad (5)$$

becomes increasingly important. If (5) is very fast compared to (4) a racemic mixture only can result. If (4) is very fast compared with (5), *l*-mandelic acid never could predominate. Nevertheless, such cases are known. Thus McKenzie and Clough[16] report that when *l*-phenyl chlor acetic acid is treated with water or aqueous sodium hydroxide, *l*-mandelic acid results, but if it is treated with silver carbonate *d*-mandelic acid is secured. An explanation which suggested itself to us and which was in accord with the face centered addition theory, was that a third independent reaction was occurring which involved two inversions. Thus if the face of the asymmetric carbon atom opposite to the chlorine were absorbed on some surface, the carbon-chlorine bond would be weakened, causing the dissociation of chloride ion and inversion. Hydroxide ion could now add, again causing inversion and releasing the molecule from the

[15] H. Menke, Phys. Zeits. **33**, 593 (1932).

[16] Alex McKenzie and G. W. Clough, J. Chem. Soc. (London) **95**, 777 (1909).

surface. The net result would be the production of *l*-mandelic acid from *l*-phenyl chlor acetic acid. Thus

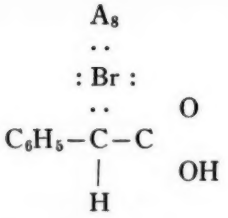
$$l\text{-}C_6H_5CHClCOOH + \text{wall} \rightarrow d\text{-wall complex} + Cl^- \quad (6)$$

$$d\text{-wall complex} + OH^- \rightarrow l\text{-}C_6H_5CHOHCOOH.$$

No optically active phenyl chlor acetic acid was available to us but the corresponding brom compound was. This had been previously investigated by McKenzie and Walker,[17] who found the action of silver carbonate on the brom compound to be similar to its action on the chlor compound. Water, however, produced a mandelic acid which was slightly dextro rotatory. Accordingly, we dissolved some phenyl brom acetic acid in water, divided the sample into two parts, and to one part added powdered silica. Both samples were then shaken in a thermostat kept at 25° for several days. The clear sample checked the observation of McKenzie and Walker, but that to which the silica had been added was levo rotatory.

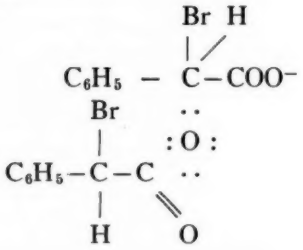
So far, there are then two ways in which a racemic mixture results; (a) reaction (5) is very fast compared to reactions (4) and (6); (b) reactions (4) and (6) have the same speed; in which case the velocity of reaction (5) is not critical. For phenyl brom acetic acid it is obvious that reaction (5) is slow enough so that we can determine that (4) is faster than (6). The addition of silica merely made (6) faster than (4). In the phenyl chlor acetic acid reaction (6) must be faster than (4).

We can now interpret the function of silver salts. The presence of silver ion will keep the halide ion concentration low and so prevent racemization by reaction (5). This can affect the magnitude of the final rotation but not the sign of the rotation—that is determined solely by the relative rates of (4) and (6). The addition of silver ion instead of reducing the surface will actually increase it due to the formation of silver chloride. Silver ion must therefore increase the speed of (4) more than (6). The formation of an addition compound such as



could accomplish this by decreasing the strength of the carbon bromine bond and thus increasing the speed of the homogeneous reaction.

In the above discussion we have neglected the possibility of ester and ring formation. If an ester such as



played a prominent part in this reaction, the rate law should contain the activity of this component to the second power which appears to be contrary to experiment.

The reactions of brom- and chlor-succinic acids are somewhat more complex than those of phenyl brom acetic acid. Walden[18] obtained an *l*-malic acid from *l*-chlor succinic acid when silver oxide was present, and *d*-malic acid when potassium hydroxide was used. Holmberg[8] and Bancroft and Davis[19] showed that the rotation of the malic acid produced depended upon the amount of excess silver oxide. These observations can be explained if we assume that in the presence of a small amount of silver oxide the main effect is to reduce the speed of reaction (5). Malic acid and chlor succinic acid which have the same rotation must then have opposite configurations. In the presence of a large excess of silver oxide, not only is (5) slow, but reaction (6) is increased. This is in accord with a preliminary experiment in this laboratory on the effect of powdered silica on this reaction. Holmberg has also submitted evidence for the

[17] Alex McKenzie and Nellie Walker, J. Chem. Soc. (London) **109**, 1685 (1915).

[18] P. Walden, Ber. **32**, 1833 (1899).

[19] W. D. Bancroft and H. L. Davis, J. Phys. Chem. **35**, 1251 (1931).

formation of a lactone which may hydrolyze in two different ways, producing malic acids of opposite rotations. Formally, these hydrolysis reactions correspond to reactions (4) and (6) in that inversion of configuration is produced by one substitution on the asymmetric carbon atom, and the original configuration is the result of two successive substitutions, each of which is accompanied by inversion. Various authors have considered the possibility of the lack of configurational change as being due to an even number of inversions.

In the case of the Beckmann rearrangement this theory predicts the favorable experimental conditions. Thus, if in benzophenone oxime the nitrogen oxygen bond is strong enough so that primary dissociation does not take place, it will be necessary for a substance with an unbonded electron pair, such as chloride ion, to approach the nitrogen face opposite to the apex to which the hydroxide is bonded, i.e., X in Fig. 3. However, because of the free electron pair on the nitrogen, such an ion would be subjected to a large coulombic repulsion. In a strong acid solution hydrogen ion will add to the free pair, and reduce this repulsion considerably. This is just the condition which Lachman[20] found was necessary for the rearrangement.

As a further application, consider the thermal isomerization of cis dibrom ethylene catalyzed by bromine. The usual explanation of this reaction is the addition of bromine at the double bond followed by a dissociation. Such an

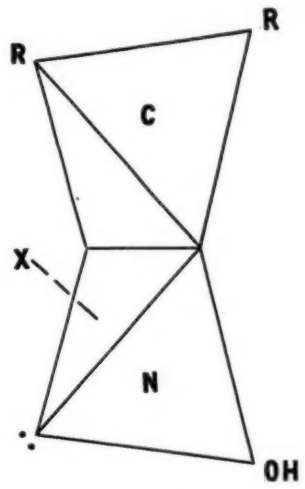


FIG. 3.

explanation cannot be correct for tetrabrom ethane is rather stable. But if bromine adds to the face of the carbon opposite to the apex at which a bromine is bound, a reaction corresponding to a Walden inversion of one of the carbons results. The new compound will be trans dibrom ethylene. This is the exact analogue of reaction (5) which has been experimentally demonstrated.

It is thus seen that this theory of chemical reactions, which is based on the energy relations involved, and on the quantum mechanical character of bonds, does satisfactorily explain the results of experiments. In its application to the experiments on the Walden inversion it leads to a direct correlation between rotation and configuration.

[20] A. Lachman, J. Am. Chem. Soc. **46**, 1477 (1924).

The Heat Capacity and Entropy of Silver Sulfate from 14 to 300°K. The Entropy of Sulfate Ion

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The heat capacity of Ag_2SO_4 has been measured from 14 to 300°K and the entropy of the salt determined by graphical integration. By coupling this value with the entropy of solution and the entropy of silver ion, the entropy of sulfate ion in aqueous solution has been evaluated.

THE determination of the entropy of silver sulfate is the first[1] of a series of investigations which, along with existing requisite data, should serve to establish the entropy of aqueous sulfate ion with a good degree of precision.

The heat capacity of Ag_2SO_4 was measured from 14 to 300°K by employing the experimental method of Latimer and Greensfelder.[1] Thomsen's[2] heat of solution was used and the free energy of solution was calculated from solubility data. The entropy of Ag^+ has been recalculated by the authors from the most recent data available. Twelve independent computations with a maximum deviation from the mean of 0.3 e.u. give $S^0_{298.1}$ of $Ag^+ = 18.3$ e.u.

Material

Silver sulfate of C.P. quality was recrystallized twice from concentrated H_2SO_4. The salt was washed and then ignited to 400°C to insure the absence of occluded H_2SO_4. A portion of the sample fused to a clear pale yellow liquid. The sample showed an Ag content (by precipitation of AgCl) of 69.11 percent, whereas theoretical is 69.19 percent. It is undoubtedly purer than the analysis indicates. Specific heat measurements were made on a sample weighing 257.444 g. (0.82562 mols).

Measurements

The molal heat capacity values fall on a smooth curve which has several points of double inflection. These points of inflection undoubtedly represent an actual property of the salt since the results are reproducible to ±0.05 percent. Moreover, $CaC_2O_4.H_2O$[1] which was measured in the same calorimeter and with the same $R-T$ scale did not exhibit such a phenomenon. The experimental results are presented in Table I and shown graphically as a function of $\log T$ in Fig. 1. The temperature intervals employed in various regions were as follows: below 30°K, about 3° per run; 30 to 200°K, about 5° per run; above 200°K, from 5 to 8° per run.

Entropy of Silver Sulfate

The entropy of Ag_2SO_4 was obtained by graphical integration of the expression $S = \int_0^{298.1} C_p d \ln T$

Table I.

T°K	Molal C_p	T°K	Molal C_p	T°K	Molal C_p
14.60	2.12	78.74	17.43	160.89	24.49
16.18	2.22	82.89	17.96	166.26	24.81
18.61	3.44	87.18	18.45	171.72	25.18
21.76	4.64	91.44	18.92	177.95	25.77
25.32	5.73	95.96	19.38	184.45	26.01
28.46	6.61	100.89	19.92	191.52	26.41
32.31	7.76	105.77	20.33	198.96	26.84
36.77	9.15	110.29	20.80	206.62	27.34
40.90	10.42	114.97	21.06	213.81	27.57
44.78	11.49	119.80	21.52	220.94	27.88
49.11	12.52	124.38	21.87	229.02	28.23
53.62	13.28	128.87	22.19	236.88	28.52
57.41	13.94	133.34	22.43	245.44	28.81
61.46	14.69	138.00	22.84	255.06	29.35
65.87	15.17	142.79	23.18	265.41	29.89
70.03	16.20	147.34	23.61	275.77	30.43
73.84	16.83	151.74	23.80	285.24	30.80
75.50	16.98	156.15	24.17	296.20	31.36

[1] Measurements on Hg_2SO_4, $CaSO_4 \cdot 2H_2O$ and $BaSO_4$ are yet unpublished. For complete reference to the general theory and previous work, see the authors, J. Am. Chem. Soc. **55**, 971 (1933).

[2] Thomsen, *Thermochemistry*, p. 52. Longmans Green and Co., 1908. Translated by K. A. Burke.

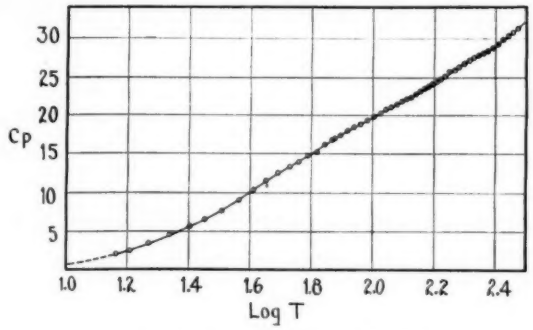

FIG. 1. The heat capacity of Ag_2SO_3.

from the curve shown in Fig. 1. The curve was extrapolated below 14°K by means of the Debye T^3 rule, $\theta = 88.01$. A summary of the entropy calculations is given in Table II.

TABLE II.

0–14°K	Extrapolation	0.624 e.u.
14–298.1°K	Graphical	47.134 e.u.

Entropy at 298.1°K of $Ag_2SO_3 = 47.76 \pm 0.05$ percent.

HEAT OF SOLUTION

Thomsen[2] gives ΔH of solution at 18°C as 4480 cal. This value was corrected to infinite dilution by means of a value[3] based on the similarity of Ag_2SO_4 and K_2SO_4 solutions. This was then corrected to 25°C by employing the partial molal heat capacities of Randall and Rossini.[4] We have then: $Ag_2SO_4(s) = Ag_2SO_4(aq)$; $\Delta H^0_{298.1} = 4207$ cal.

FREE ENERGY OF SOLUTION

Chloupek and Danes[5] find that a saturated solution of Ag_2SO_4 at 25°C is 0.026888 m. This agrees well with the solubility of Harkins and others.[6] We have used 0.533[7, 8] for the corresponding activity coefficient. The free energy of solution is given by $\Delta F^0_{298.1} = -1363.8 \log [4 \times (0.533 \times 0.02689)^3] = 6722$ cal.

ENTROPY OF SULFATE ION

Substituting in the equation $\Delta S^0 = (\Delta H^0 - \Delta F^0)/T$, we have for the reaction, $Ag_2SO_4(s) = 2Ag^+ + SO_4^{--}$ (hypothetical one molal solution); $\Delta S^0_{298.1} = -8.4$, which yields in turn, by application of the third law: $-8.4 = 2 \times 18.3 + S^0_{SO_4^{--}} - 47.8$; $S^0_{298.1}$ of $SO_4^{--} = 2.8$ e.u.

In spite of the uncertainty in correcting Thomsen's[2] heat of solution to the standard state at 25°C, we regard 2.8 as being reliable to 1.0 e.u.

[3] Lange and Streeck, Zeits. f. physik. Chemie **A157**, 1 (1931).

[4] Randall and Rossini, J. Am. Chem. Soc. **51**, 323 (1929).

[5] Chloupek and Danes, Collection of Czeckoslovak Chemical Communications **4**, 124 (1932).

[6] Harkins, J. Am. Chem. Soc. **33**, 1813 (1911); other references in this paper. Hill and Simmons, J. Am. Chem. Soc. **31**, 821 (1909); Zeits. f. physik. Chemie **67**, 594 (1909). Rothmund, Zeits. f. physik. Chemie **69**, 523 (1910). Drucker, Zeits. f. anorg. Chemie **28**, 362 (1901).

[7] Lewis and Randall, *Thermodynamics and Free Energy of Chemical Substances*, McGraw-Hill, New York, 1923.

[8] Hass and Jellinek, Zeits. f. physik. Chemie **A162**, 167 (1932). 0.533 compares favorably with values obtained for similar salts by these workers.

LETTERS TO THE EDITOR

In response to requests from our contributors, and after a canvass of the opinions of the Editorial Board, the Journal of Chemical Physics wishes to announce that a "Letters to the Editor" section will be carried by the Journal. This section will accept reports of new work, provided they are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual page charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Isotopic Fractionation of Water by Distillation and by Adsorption*

The discovery[1] that water in which the heavier isotopes of H_2 and O_2 have been concentrated by electrolysis has a higher boiling point than normal water shows that it must be possible to fractionate water by distillation. To demonstrate this, 10 liters of water having a specific gravity of 1.000053 were distilled at atmospheric pressure in a still provided with a 35-foot rectifying column. An initial distillate of 200 ml and the final residue of 100 ml were compared as to density and found to differ by 64.9 parts per million, the residue having increased by 53.3 parts and the distillate having decreased by 13.2 parts. Distillation fractionation is thus possible and should find practical application in combination with electrolysis fractionation.

The adsorptivity of water by porous materials or powders should vary with its isotopic composition and it should therefore be possible to fractionate water by adsorption. To demonstrate this 300 g of activated charcoal was allowed to stand for three weeks immersed in 500 g of water having a specific gravity of 1.000053. The supernatant water (176 ml) and the last 123 ml of water which could be expelled from the charcoal by heating in vacuo at 500°C were compared as to density and found to differ by 12.4 parts per million, the supernatant water having decreased by 6.5 parts and the adsorbed water having increased by 6.7 parts.

The specific gravities reported above were determined on carefully purified samples of water and are based upon normal water taken as unity.

EDWARD W. WASHBURN
EDGAR R. SMITH

Bureau of Standards,
Washington, D. C.,
May 15, 1933.

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